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SYMPOSIUM ON FLOW PROPERTIES OF ADMIRALTY FUEL OILS

SECOND SESSION

WITH Dr C. M. Cawley in the chair, the following papers were presented in summary:

THE MEASUREMENT OF FLOW PROPERTIES BY CO-AXIAL CYLINDER VISCOMETER *

Prepared by E. S. SELLERS † (Fellow) and D. WYLLIE (Fellow) ‡ and presented by E. S. SELLERS

INTRODUCTION

WHEN a fluid possesses truly Newtonian viscous properties it has a unique viscosity at any temperature, irrespective of the shearing stresses or shear rates at which the viscosity is measured or of the time for which shearing takes place. A variety of viscometers is currently used to determine the viscosity of such fluids. Furnace fuel oils at atmospheric storage temperatures behave in a markedly non-Newtonian manner and exhibit a range of apparent viscosities with variation in shear stress, shear rate, or time of shearing. It is therefore necessary to employ an instrument in which either the shear stress or shear rate to which the fluid is subjected can be closely controlled at any desired level throughout the time of shearing.

Margules [1] first derived an expression for the calculation of the viscosity of a fluid contained in a narrow annular space between two co-axial cylinders, one of which is rotated; Couette [1] experimented with such a system, the first practical viscometer being evolved by Searle [1] at a considerably later date. If the radii r_1 and r_2 of the cylinders are both considerably greater than $r_1 - r_2$, (*i.e.* the width of the annular space between the two) and the cylinders are constructed in such a manner as to minimize end effects, viscosities can be measured with a high degree of control over the conditions of shear. These instruments have therefore been extensively used in both the field and laboratory work described in this symposium.

APPARATUS

Both constant shear-stress and constant shear-rate instruments have been employed (Fig 1). The constant shear-stress instruments are of the type described by Mooney and Ewart,[2] which, in order to control the end effects, have coni-cylindrical inner and outer cylinders (not plain cylinders) as shown in Fig 2. Constant shear stress is obtained by applying constant load to one of the pans *g*; this causes the spindle *f* and inner cylinder *b* to rotate on the bottom bearing *c*. The inner cylinder is held in position by the bearing *d*

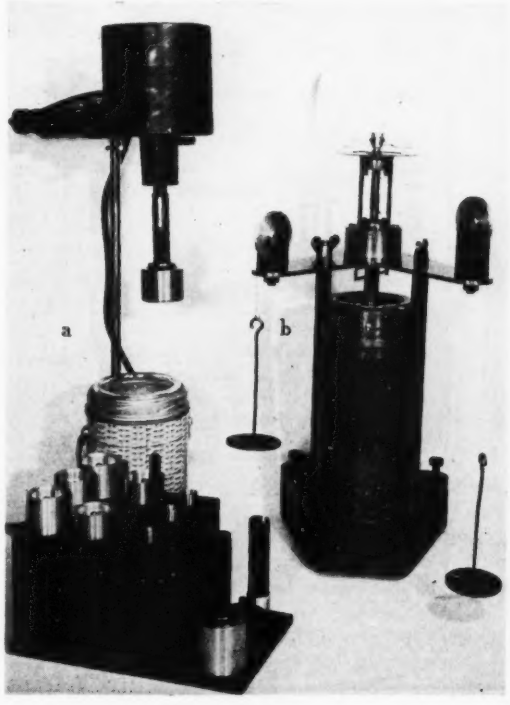

FIG 1

TYPICAL CO-AXIAL CYLINDER VISCOMETERS

(*a*) Constant shear rate (Ferranti portable viscometer)
(*b*) Constant shear stress

* MS received 4 December 1959. † University College, Swansea. ‡ Admiralty Oil Laboratory, Brentford, Middlesex.

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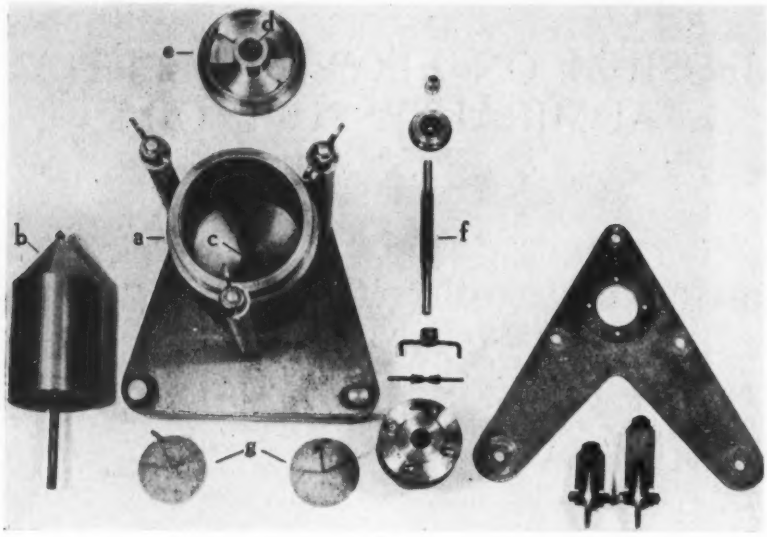

FIG 2
DETAILS OF CONSTANT SHEAR STRESS VISCOMETER

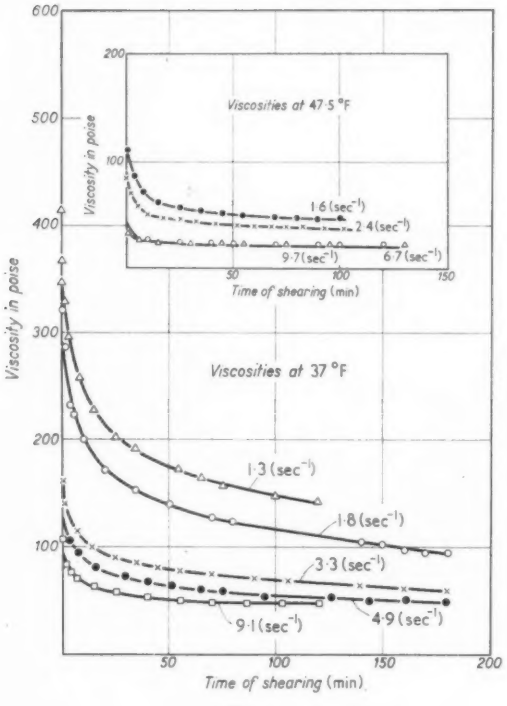

FIG 3
CHANGE OF VISCOSITY WITH TIME AT CONSTANT RATE OF SHEAR

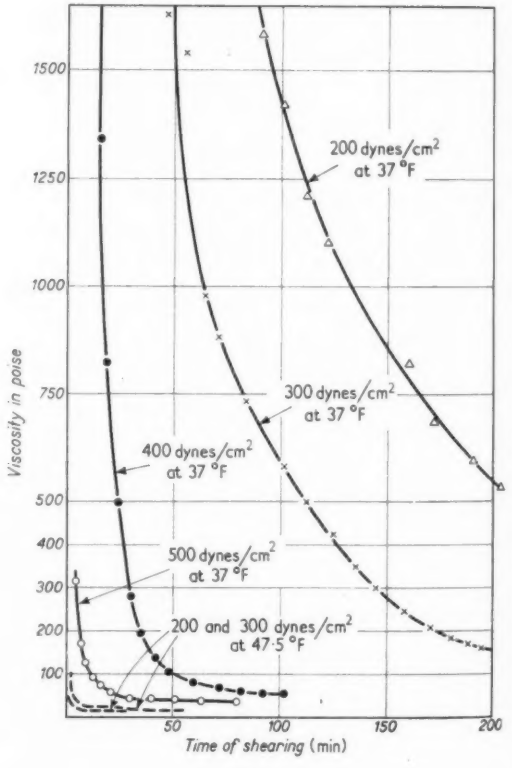
Viscosity in poise
Time of shearing (min)
200 dynes/cm² at 37 °F
300 dynes/cm² at 37 °F
400 dynes/cm² at 37 °F
500 dynes/cm² at 37 °F
200 and 300 dynes/cm² at 47·5 °F

FIG 4
CHANGE OF VISCOSITY WITH TIME AT CONSTANT SHEAR STRESS

in the centre of the outer cylinder cap, *e*. The required amount of oil to be tested is poured into the outer cylinder *a*, before the instrument is assembled.

In the constant rate-of-shear instruments, one cylinder is rotated at constant speed, and the force exerted on the other cylinder is measured. The first instruments of this type employed by panel members were specially made in their laboratories; later it was found that one commercially available, the Ferranti Portable Viscometer, would meet the requirements. This instrument can be operated at a range of rates of shear by varying the outer and inner cylinder sizes; also three speeds can be selected, giving three rates of shear for each pair of cylinders. It is proposed to use this instrument in the new Admiralty specification pumpability test. A sectional drawing of the viscometer is included in Appendix II of the paper by Ackroyd, Hosking, and Lowe.[3]

TYPICAL RESULTS

Fig 3 shows the type of viscosity/time-of-shearing curves which are obtained on fuels at temperatures at which they exhibit marked non-Newtonian properties. At the higher rates of shear the viscosity decreases rapidly to a near constant figure. At the lower rates of shear the apparent viscosity is higher and takes much longer to reach a near constant value. The viscosity may continue to fall slowly throughout many hours of continuous shearing.

Viscosity/time-of-shearing curves for the same oil at the same temperature and in the same condition before shearing commenced are shown in Fig 4. At high shear stress well above the yield value of the oil, the viscosities rapidly attain nearly constant values. At lower shear stresses near to the yield value, little movement of the rotating cylinder of the viscometer takes place at first, and for some time the apparent viscosities are very high. The cylinder then begins to turn at an increasing rate, which eventually tends to a constant speed. If the applied shear stress is lower still, no measurable movement of the viscometer may occur, the applied stress being less than the yield value of the oil. An alternative method of presenting these results is to plot rate of shear against time for constant stress, as in Fig 5. This shows clearly the negligible amount of movement which takes place in the early stages at the lower shear stresses.

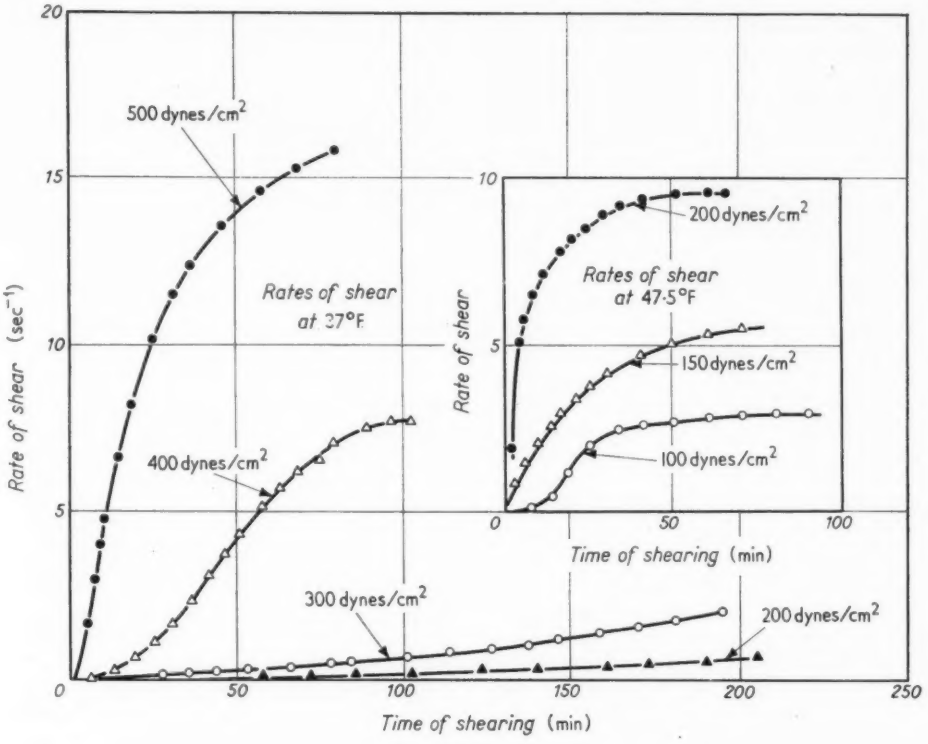

FIG 5

CHANGE OF SHEAR RATE WITH TIME AT CONSTANT SHEAR STRESS

At higher temperatures these same oils tend towards and eventually behave as Newtonian fluids. Fig 5 reduces to a series of lines parallel to the time axis, one for each shear stress.

PROBABLE STRUCTURE OF FURNACE FUEL OIL

The fuels under discussion are residual fuels cut back with middle distillates to give a blend whose viscosity at 122° F does not exceed 300 sec Redwood No. 1 or, as in the current Admiralty specification, 200 sec Redwood No. 1. This is decidedly less viscous than many commercial fuels. As a first approximation it may be said that they consist of an oil fraction, wax, resins, and asphaltenes, these being the fractions which can readily be obtained by laboratory extraction methods.

These separations are inevitably somewhat arbitrary, as each contains a range of compounds of similar structure. Thus the waxes are essentially the higher boiling members of the paraffinic components of the oil fraction. The difference between asphaltenes and resins was originally given by Marcusson [4] in terms of solubility in petroleum ether, the asphaltenes being the less soluble members of this family, the extreme members of which are the very insoluble carboids containing a very high carbon/hydrogen ratio, which are liable to be found in residuals, especially cracked residuals.

Sachanen [5] stated that asphaltenes are dispersed colloidally in petroleum products due to peptization by absorbed resins and heavy polycyclic hydrocarbons, whereas neutral resins form true solutions. He went on to state that asphaltenes are dispersed in petroleum oils either colloidally or in suspension and, in the presence of waxes, are the cause of the heterogeneous structure. The excess petroleum wax above saturation forms the microcrystalline structures modified by the colloidal structure formed by the asphaltenes. Work by Cawley, Ackroyd, Aubrey, and Lowe,[6-8] referred to in the paper by Ackroyd, Hosking, and Lowe, presented in this symposium, has examined these points. They found that wax-free oil generally behaved in a Newtonian manner but oil containing wax was liable to develop non-Newtonian properties whether or not asphaltenes and resins had been removed.

In an aged fuel, *i.e.* one which has been in unheated storage for at least a year, the structure can be visualized as consisting of aggregates of wax crystallites modified by and in association with micelles of asphaltenes. At storage temperatures this structure is forming in a viscous fluid, and a considerable time is required for it to develop fully. Shearing in a viscometer or in a pipeline breaks up these aggregates. The viscosity of furnace fuel oil thus depends not only on the conditions of shear but also on time.

THE VISCOSITY OF FURNACE FUEL OILS [9,10]

At temperatures at which these behave as true Newtonian fluids this can be expressed by

$$p = \mu S \quad . \quad . \quad . \quad . \quad (1)$$

where μ is the viscosity, a constant for any given temperature and for all values of the applied shear stress, p, and rate of shear S.

A simple type of non-Newtonian fluid is a Bingham plastic, in which the fluid has a yield value below which flow cannot occur. For this

$$p - p_y = \eta S \quad . \quad . \quad . \quad . \quad (2)$$

where p_y is the yield value and η a coefficient of rigidity or plastic viscosity.

The apparent viscosity μ_a which is obtained in a viscosity determination is

$$\mu_a = \frac{p_y}{S} + \eta \quad . \quad . \quad . \quad . \quad (3)$$

Many non-Newtonian fluids show an experimental relationship between p and S as follows:

$$p = K S^n \quad . \quad . \quad . \quad . \quad (4)$$

where K and n are constants at a given temperature. The apparent viscosity is given by

$$\mu_a = \frac{K}{S^{(1-n)}} \quad . \quad . \quad . \quad . \quad (5)$$

All the above relate to fluids which are not time-dependent, *i.e.* they have one apparent viscosity at any temperature for any given shear stress or rate of shear. The fluids under discussion are time-dependent and non-Newtonian, and the apparent viscosity decreases with time of shearing.

Attempts have been made to consider the flow mechanism as a rate process, largely by Eyring and his collaborators [11] and some work on these lines has been done at the Admiralty Oil Laboratory.[12]

The problem was to apply viscometric data to the flow of fuel oil in round pipes, where the shear stress at the pipe wall is given by

$$P_w = \frac{\Delta P r}{2L} \quad . \quad . \quad . \quad . \quad (6)$$

where ΔP is the pressure drop, r the radius, and L the length of the pipe. In addition

$$P_w = f(S, t) \quad . \quad . \quad . \quad . \quad (7)$$

the nature of this function being unknown.

The literature available at the time of the earlier large-scale pumping trials related mainly to fluids which are not time-dependent. Fortunately, examination of the results of the pumping trials showed that once steady-flow conditions had been set up in the pipe, the " pipe viscosity," *i.e.* the apparent Newtonian

viscosity of the oil in the pipe, derived from measurements of pressure drop and rate of flow, was similar to the "equilibrium viscosity" of the oil in a co-axial cylinder viscometer measured at the rate of shear presumed to exist in the pipe. The term "equilibrium viscosity" was used to describe the comparatively constant viscosity level reached after the shearing in the viscometer until the viscosity no longer decreased rapidly with time. This subject is dealt with in detail in the paper on the large-scale pumping trials.[13] In later work at the Admiralty Oil Laboratory, in the pumping rig discussed later in this symposium,[14] the mean residence times of the oil in the pipe were much less than in the field pipelines. It appears that in these circumstances pipe viscosities should be compared with those obtained in a viscometer after a correspondingly shorter time of shearing.

The limited field trials carried out with a pipeline filled with gelled oil suggested that the pipe viscosities from start-up until steady flow is attained are similar to those obtained in a constant shear-stress viscometer. Work on the pumping rig has shown that this probably holds from start-up even when no measurable flow occurs for some time in the pipe.

The empirical approach on the basis of equilibrium viscosity is essentially an elimination of the time-dependent behaviour of the system from the calculation. A complete synthesis of the rheological properties of a fluid which exhibits thixotropic behaviour must take into account any time effects in the system. Such an approach has been suggested by Billington,[12] following experiments at the Admiralty Oil Laboratory, with both constant shear-stress and constant shear-rate types of viscometers.

Billington assumes that the thixotropic behaviour of the wax-containing oils can be attributed to a suspension of deformable particles in a Newtonian base liquid. The deformable particles are aggregates of wax-crystallites; the size of the aggregates increases with increasing time of storage. The effect of an applied shearing stress is to produce a time-dependent breakdown of the deformable particles. The individual wax crystallites are considered to be the smallest products of breakdown. The liquid consisting of the soluble wax in the Newtonian base liquid is referred to as the residual liquid and is assumed to be Newtonian in behaviour. The presence of the deformable particles produces a resistance to flow, such that there is a limiting value of the applied stress below which flow does not occur. This limiting value of the applied shearing stress is referred to as the yield stress, or yield value, and is defined as the maximum force per unit area that the deformable particles can sustain in shear without flow occurring, *i.e.* the yield value is a measure of the strength of the structure. After an infinite time of shearing it is assumed that the system has been completely transformed to the residual liquid. The apparent viscosity at a given time t must therefore be regarded as a function of the following quantities.

$$\mu t = f[p(t), S_t, p_y(t), p_e(t), \mu_R] \quad . \quad . \quad (8)$$

where $p(t)$ = applied stress at time t;
S_t = rate of shear at time t;
$p_y(t)$ = yield stress at time t;
$p_e(t)$ = stress system producing elastic effects at time t;
t = time of shearing;
μ_R = viscosity of the residual liquid.

The internal structure may also behave like a system of elastic elements, in which case it is assumed that the

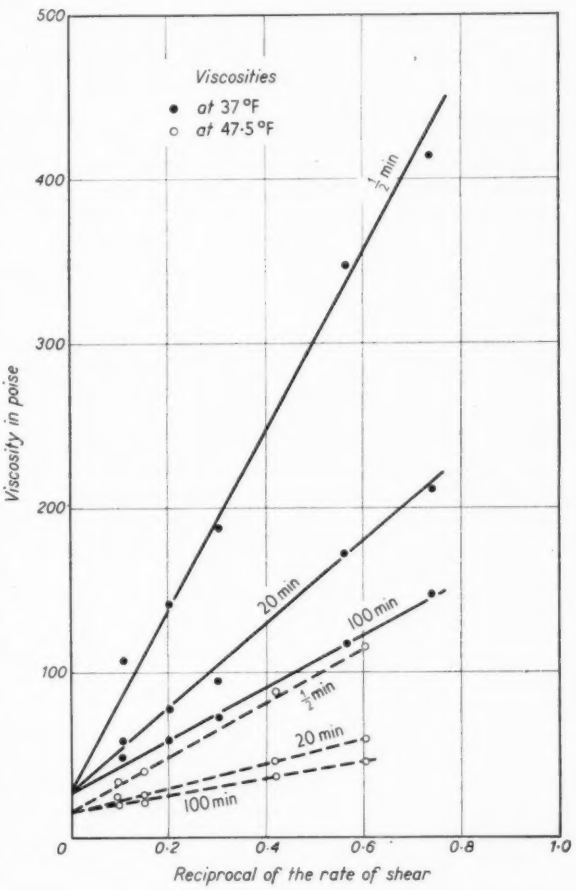

FIG 6
VARIATION OF VISCOSITY WITH RATE OF SHEAR

elastic and viscous stress systems are independent, *i.e.* the applied stress may be expressed in the form

$$p(t) = p_V(t) + p_e(t) \quad . \quad . \quad . \quad (9)$$

where $p_V(t)$ is the stress system producing viscous flow,

and $p_e(t)$ the stress system producing the elastic effects. For viscous flow we have

$$p_V(t) = p_R(t) + p_y(t) = \mu_t S_t \quad . \quad (10)$$

where $p_R(t)$ is the shearing stress per unit area producing viscous flow of the residual liquid and is related to the viscosity of the residual liquid by the relation

$$p_R(t) = \mu_R S_t \quad . \quad . \quad . \quad (11)$$

Combining (9), (10), and (11) one obtains the relation

$$p(t) - p_e(t) = \mu_R S_t + p_y(t) = \mu_t S_t \, . \quad (12)$$

For constant rate of shear $S_t = S$ so

$$(\mu_t - \mu_R)S = p_y(t) \quad . \quad . \quad (13)$$

The viscosity/time-of-shearing curves at constant rates of shear shown in Fig 3 give the viscosity *v.* reciprocal rates of shear, *i.e.* μ_t *v.* $1/S$ graphs of Fig 6. It will be seen that when $1/S = 0$, *i.e.* the rate of shear approaches infinity, the graphs converge at μ_R, the residual viscosity of the fluid at the appropriate temperature. The slope of the lines which from equation (13) should equal the yield value decreases with time of shearing, and in the fully sheared structureless condition will be parallel to the base line, the yield value being zero.

The next step is to insert in equation (13) the value for μ_R, the viscosity of the residual liquid which has been obtained graphically (Fig 6), and to evaluate $p_y(t)$ for a variety of rates of shear and times of shear. It is found that the independent viscosity/time-of-shearing curves of Fig 3 combine to give within experimental error a single curve for the decay of $p_y(t)$, the yield stress, with time of shearing t. Experimental results obtained using a constant shear-stress viscometer are shown in Figs 4 and 5. At low values of shear stress there was an appreciable delay time before continuous movement of the cylinder occurred. This situation has been further analysed by Billington [12] in terms of the elastic and viscous stress systems assumed to exist. From measurements of the initial delay time in the viscometer, a prediction can be made of the delay which would occur before movement takes place when a pipeline full of oil in the same condition is pumped.

ACKNOWLEDGMENTS

The authors are indebted for permission to publish this paper to the Board of Admiralty, who are not, however, responsible for the opinions expressed.

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THE DEVELOPMENT OF A TEST TO PREDICT THE PUMPABILITY OF ADMIRALTY FURNACE FUEL OILS *

Prepared by G. C. ACKROYD †, Miss D. E. M. HOSKING †, and A. G. LOWE †
and presented by G. C. ACKROYD

SUMMARY

The work briefly described in this paper covers the co-operative activities of a number of laboratories over several years. The object of the work was to devise a laboratory test to enable the flow properties of Admiralty furnace fuel oil to be specified. Having determined, by a pour point procedure, the condition of oils in Admiralty storage, a test known as Method VII based on pour point was developed to enable the condition of oils after prolonged storage to be predicted at the time of preparation of the oil at a refinery.

Further work, including full-scale pumping trials in a pipeline of 14- to 18-inches diameter, showed that the pumping characteristics of an oil in storage could best be evaluated by a test involving the determination of the viscosity of the oil. A survey was therefore made of the flow properties of oils in storage at Admiralty depots using a coaxial cylinder viscometer. Based on this data, heat treatment procedures were investigated and eventually Method XV was evolved which satisfactorily predicted the viscosities which the oils attained in Admiralty storage. Finally, storage trials were made over two and half years on freshly prepared oils, when it was found that towards the end of the second year the viscosities of the stored oils approached those predicted by Method XV.

INTRODUCTION

Since 1950 the Admiralty Fuel and Lubricants Advisory Committee has carried out extensive investigations into the flow properties of residual fuel oils. The need for the work arose from the observation that the flow properties of some residual fuel oil deteriorated during the storage of the oils. This deterioration appeared to be due to the presence of asphaltenes and wax in the oils, which, under the influence of slow changes in temperature, formed structures in the oil affecting the flow properties.

The object of the present work was to devise a laboratory test to enable the "Ultimate Pumpability" of a waxy, residual fuel oil to be predicted. The Ultimate Pumpability is defined as the lowest degree of pumpability that the oil may reach in storage for any period up to five years.

The work falls into two parts:

(1) To devise a laboratory method of treating a residual fuel oil so that it will acquire the condition of Ultimate Pumpability.

(2) To devise a laboratory test to enable the pumpability of an oil in any conditions to be measured.

POUR POINTS OF OILS IN STORAGE

In the early stages of this work, and lacking any better criterion, the pour point of an oil was taken as a measure of the temperature at which an oil is likely to become unpumpable. Both the IP and the ASTM had developed a procedure in which the formation of a structure in the oil is accelerated by artificial heat treatment and the pour point of the treated oil is taken as an indication of the handling characteristics of the oil at low temperatures.

In order to find out the conditions of oils in storage, a most important step if a test is to be developed to simulate this condition, the concept of "as received" pour point was introduced. Samples of oil that had been in storage in Admiralty depots for a number of years were brought to the co-operating laboratories and their pour points determined using the standard IP procedure but omitting the preheating stage. The pour point so determined was known as the "as received" pour point; "as received" pour points on some oils that had been in storage for many months are given in Table I.

IP (UPPER) POUR POINT

The IP (Upper) Pour Point was considered as one possible method of predicting the behaviour of oils on aging. Table I gives IP (Upper) Pour Points on a number of oils soon after they had been put into storage and also after many months of storage. For oils A to F, of Middle East origin, the IP (Upper) Pour Points before storage are in reasonable agreement with the "as received" pour points after protracted storage, but for oils H, I, J, and K, of Western Hemisphere origin, the IP (Upper) Pour Points before storage were below the "as received" pour points after storage.

The structure that builds up in oils during storage can be largely destroyed by heating to 200° F or above, and the oils then revert to a low pour point condition. In some cases subsequent treatment by

* MS received 29 October 1959.

† Dept. of Scientific and Industrial Research.

the IP (Upper) Pour Point procedure fails to produce a high pour point. Subsequently, a similar problem was found with oils freshly blended at a refinery. In some cases only after the oils had aged for a number of weeks would the IP (Upper) Pour Point procedure induce a high pour point condition in the oil. Other freshly prepared oils responded at once to the IP (Upper) Pour Point procedure.

The problem to be solved was how to pre-treat an oil, at the time of its preparation at a refinery, so that it would simulate the flow properties of the same oil after prolonged storage. It was not possible to take freshly prepared oils, subject those to various pre-treatments, and compare the pour points of these treated oils with the " as received " pour points of the oils after prolonged storage. This would have taken too long. As a compromise, as indicated above, the " as received " pour points of aged oils were measured and compared with IP (Upper) Pour Points on the same oils that had been heated to 200° F or above to destroy the structure developed by age.

At a later date freshly prepared oils were examined by various pre-treatment procedures and the oils subsequently stored to see if the " as received " pour points would increase to that predicted by the pre-treatment procedure. The results of this work are dealt with later in this paper.

DEVELOPMENT OF METHOD VII

It was known from the work of the Anglo-Iranian Oil Co that pour points higher than the IP (Upper) Pour Point could be obtained by introducing an element of shock chilling into the standard IP Pour Point procedure. Oils of the types indicated in Table I were therefore subjected to various forms of shock chilling and heat treatment in order to find a method generally applicable to the range of oils in which the Admiralty were interested. Over 1000 pour point tests were made in which various types of apparatus (metal or glass), methods of shock chilling, various reheat temperatures, etc., were examined. Extensive co-operative tests between laboratories were made to determine repeatability and reproducibility. Finally, after passing through six major modifications, a method known as Method VII was evolved.

In Method VII the oil is heated to 170° F, cooled to 120° F in air, and then shock chilled to 0° F in a bath at −30° F. The shock-chilled oil is then reheated to some temperature in the range 70° to 140° F and the pour point of this reheated oil determined as it cools. The highest pour point obtained as a result of the individual experiments on the reheated oils is known as the " Flow Point." Method VII results are also included in Table I. Details of Method VII, which has been included in the Admiralty furnace fuel oil specification, are given in Appendix I.

TABLE I

Pour Points of Oil Sample

	Middle East oils						Western Hemisphere oils						
Oil	A	B	C	D	E	F	G	H	I	J	K	L	M
Age of sample, months	38	36	38	36	38	41	34	40	40	39	39	38	72
" As received " pour point, ° F	50	55	55	60	55	60	30	35	45	35	30	−10	0
IP (Upper) Pour Point, ° F (at time of going into storage)	—	65	60	65	65	55	30	25	40	20	30	−10	0
IP (Upper) Pour Point, ° F (after storage)	50	60	65	60	60	60	15	15	15	20	20	−20	−10
Method VII													
Heat treatment temperature, ° F 70	—	—	—	—	—	—	—	—	20	—	20	—	—
80	—	—	—	—	—	—	—	—	30	—	15	—	—
90	50	60	60	60	60	70	10	5	25	20	10	−15	−5
105	60	70	70	75	70	70	15	5	20	20	20	−15	−5
120	55	75	70	75	70	80	15	10	20	25	25	−15	−5
140	—	70	70	70	70	70	—	20	—	30	10	−10	—
160	—	—	—	—	—	—	—	0	—	—	—	—	—
Flow point, ° F	60	75	70	75	70	80	15	20	30	30	25	−10	−5

CHOICE OF PRE-TREATMENT PROCEDURE

The choice of a procedure in which the oil is first heated to some predetermined temperature before shock chilling, and then subsequently reheated to a particular temperature before finally cooling to de-

termine the pour point, is not entirely arbitrary. Fig 1 illustrates the range of pour points an oil may exhibit according to the temperature to which the sample is reheated after shock chilling. By reheating to 140° F the oil is obtained in the low pour point condition and Fig 2 (*a*) is a photomicrograph showing the condition of the wax crystals in the oil; by reheating to 105° F the oil is obtained in a high pour point condition and Fig 2 (*b*) shows the condition of the wax after this treatment. In the low pour point condition there are clusters of wax crystals about 30 microns in diameter; in the high pour point condition the resolution of the microscope is not sufficient to show the presence of any crystalline material. However, the X-ray-diffraction picture[4] of these two samples, given in Fig 3, indicates that both contain approximately the same amount of crystalline material, so that in the low pour point condition crystals less than about 1 to 2 microns must be present. In oils that have aged for long periods in storage very large aggregates of wax are often present (up to 100 microns), but it is not possible to say if oils in the low pour point condition, as illustrated by Fig 2 (*a*), and naturally-aged oils, contain the same amount of wax in the form of these large aggregates. It seems more likely that in naturally-aged oils the state of crystallization of the wax is mainly between the extremes represented by Figs 2 (*a*) and 2 (*b*).

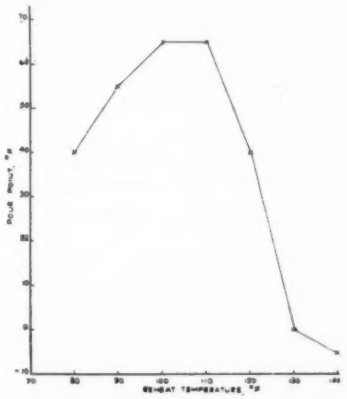

FIG 1

VARIATION OF POUR POINT WITH REHEAT TEMPERATURE

The physical properties of heat-treated oils are largely governed by interactions of asphaltenes, resins, and wax. Asphaltenes are defined as material insoluble in light petroleum or heptane. Resins are defined as that material which is adsorbed by alumina from a deasphalted oil and cannot be removed by subsequent extraction of the alumina with light petroleum. Wax is defined as that material in an asphaltene and resin-free oil which is insoluble in methyl-ethyl ketone. The data in Fig 4 show the variation in pour point with reheat temperature for: (1) a sample of the original oil; (2) the same oil free from asphaltenes; (3) the same oil free from asphaltenes and resins, (4) the same oil free from asphaltenes, resins, and wax. The marked influence of the resins on the pour point is evident.

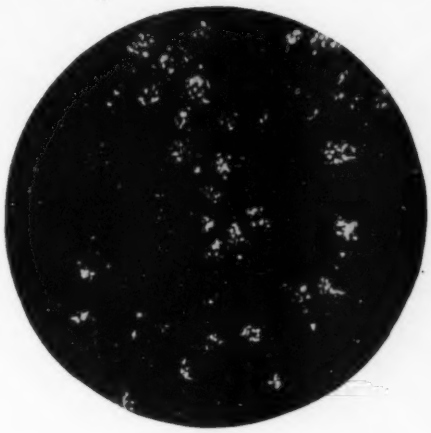

FIG 2 (*a*)

PHOTOMICROGRAPH (×320) OF RESIDUAL OIL IN LOW POUR POINT CONDITION

(Pretreatment temperature 140° F)

FIG 2 (*b*)

PHOTOMICROGRAPH (×320) OF RESIDUAL OIL IN HIGH POUR POINT CONDITION

(Pretreatment temperature 105° F)

A more careful study of these same oils, in which they were tested in a coaxial cylinder viscometer both in the high and low pour point conditions, gave the results in Fig 5. In the low pour point condition there

is little difference between the viscosities of the original oil and the same oil after removal of asphaltenes. In the high pour point condition the oil without the

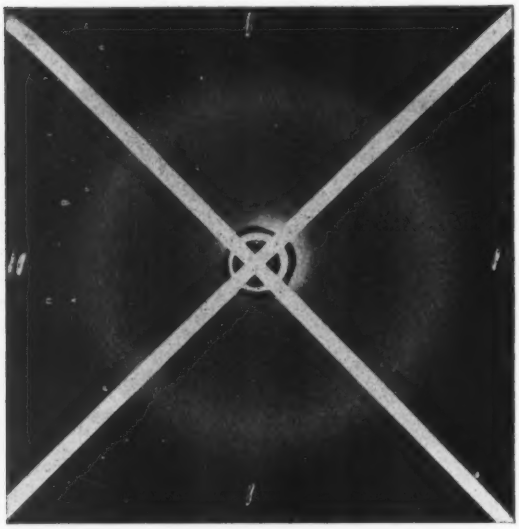

FIG 3

RESIDUAL FUEL OIL X-RAY DIFFRACTION PATTERN

(i) Oil in low pour point condition
(ii) Oil in high pour point condition

asphaltenes is only slightly more viscous than when in the low pour point condition, but when the asphaltenes are present and the oil is in the high

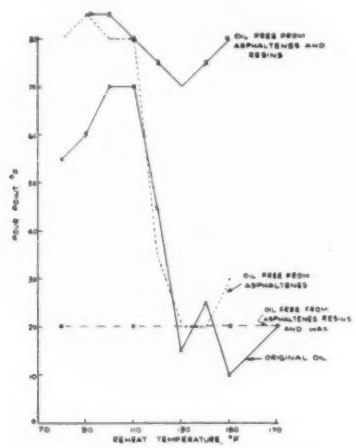
OIL FREE FROM ASPHALTENES AND RESINS
OIL FREE FROM ASPHALTENES
OIL FREE FROM ASPHALTENES RESINS AND WAX
ORIGINAL OIL
POUR POINT °F
REHEAT TEMPERATURE, °F

FIG 4

POUR POINTS OF AN OIL BEFORE AND AFTER REMOVAL OF ASPHALTENES AND WAX

pour point condition there is a very marked increase in viscosity. This seems to indicate that, in the high pour point condition, asphaltenes play a major part in the formation of structures affecting the flow properties. The removal of asphaltenes and resins gives an oil which produces very anomalous results when tested in a coaxial cylinder viscometer. It is possible

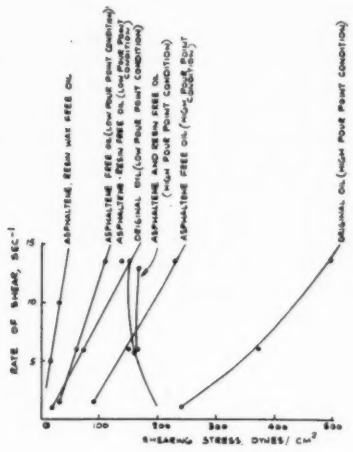
ASPHALTENE, RESIN WAX FREE OIL
ASPHALTENE FREE OIL (LOW POUR POINT CONDITION)
ASPHALTENE - RESIN FREE OIL (LOW POUR POINT CONDITION)
ORIGINAL OIL (LOW POUR POINT CONDITION)
ASPHALTENE AND RESIN FREE OIL (HIGH POUR POINT CONDITION)
ASPHALTENE FREE OIL (HIGH POUR POINT CONDITION)
ORIGINAL OIL (HIGH POUR POINT CONDITION)
RATE OF SHEAR, SEC⁻¹
SHEARING STRESS, DYNES/CM²

FIG 5

SHEARING STRESS/RATE OF SHEAR DIAGRAMS OF OIL BEFORE AND AFTER REMOVAL OF ASPHALTENES, RESINS, AND WAX

that the oil possesses a high yield value and plug-flow occurs. The oil free from asphaltenes, resins, and wax exhibits Newtonian viscous properties.

YIELD VALUE

Having developed, in Method VII, a pour point procedure which would cover immediate Admiralty requirements for a specification test, attention was turned to the yield value of an oil as a means of measuring pumpability. In this method a capillary U-tube was filled with heat-treated oil, the whole cooled to the test temperature, and the yield value of the gelled oil in the U-tube determined by application of pressure to one limb of the tube. This work is described in another paper. It was found that the repeatability and reproducibility of yield value tests were much poorer than those for pour point tests. In particular, a useful lesson was learnt, namely, that in a shock-chilling procedure, unless only a thin layer of oil is involved, the oil becomes heterogenous, and this can lead to erratic results. Moreover, it was found necessary to standardize very carefully the rate of cooling to the test temperature, usually 32° F, as this could have a very marked influence on the final yield value.

In order to be able to compare yield values obtained in the laboratory tests with the behaviour of oils in storage, actual cold weather pumping trials were then undertaken. From these many useful lessons were

learnt, and as a result both pour point and yield value were abandoned in favour of viscosity determination.

PUMPING TRIALS AND METHOD XV

Full-scale pumping trials were carried out at an Admiralty depot in several thousand feet of 14- to 18-inch diameter pipeline in which the pressure drop, as the oil flowed down the line, could be measured. At the same time as the oil was pumped, samples were taken and " as received " pour points, yield values, and viscosities in a coaxial cylinder viscometer were determined. The pumping trials are dealt with in another paper. As a result of these trials it was found that, in transporting samples from storage depots to laboratories in London and other parts of the country, considerable changes could occur in the oils, structures built up through prolonged storage being considerably modified by even relatively mild temperature changes. Transport of samples in well-lagged thermos vessels was found to be the best way of ensuring that samples would reach the laboratory in something like the same condition as at the time of sampling. However, from this time onwards most of the " as received " data were collected by taking the measuring instruments to the depot and making the measurements there.

The pumping trials also demonstrated the value of viscosity measurements, made at shearing stresses comparable to those to which oils are subjected during pumping operations, as a means of characterizing their flow properties. It was therefore decided to develop a test based on viscosity, and in order to do this an extensive investigation was made at a number of Admiralty depots of the viscosities of the oils in storage. Also, in conjunction with The British Petroleum Co and the Admiralty, viscosity changes were measured in an oil from the day of its preparation until it was several years old. At the same time as the " as received " viscosities were being determined, the oils, after heating to destroy the structure developed by age, were examined by a number of heat treatment procedures. As a result Method XV was evolved, which allows the viscosities of Admiralty furnace fuel oils to be predicted with some confidence.

METHOD XV

Method XV differs from Method VII in a number of ways, the most important being that all shock-chilling and heat treatment is carried out in brass vessels with a layer of oil only a few millimetres thick. These thin layers of oil in a metal container enable the degree of shock chilling to be substantially reduced, while at the same time allowing a wider range of oils to be handled than can be done by Method VII. Also, it was found that the rate of heat transfer to the chilling liquid had to be carefully controlled to obtain reproducible results, and to achieve this the cooling liquid in contact with the metal containers is kept agitated with wire stirrers.

Details of Method XV are given in Appendix II.

THE CONDITION OF OILS IN STORAGE

It was not until pumping trials were undertaken at an Admiralty depot that the extreme sensitivity of the structures in furnace fuel oils was appreciated. This work showed that isothermal handling of the oils from the tanks to the testing instrument was essential: moreover, it became clear that only laboratory measurements made at the temperature of the oil in the tank at the time of sampling would have any significance from the point of view of establishing the flow properties of the oil as it existed in the tank. Relatively small changes in the temperature of the sample, either by warming or cooling, were found to produce marked changes in the viscosity of the oil.

A programme of field testing was therefore undertaken so that reliable data could be obtained on the condition of oils after prolonged storage. To this end a coaxial cylinder viscometer was taken to a selected depot at intervals of one to three months. The viscometer operated at a constant rate of shear and the oils were usually tested at rates of shear of 1, 2, and 4 sec^{-1}. In most cases two samples of oil were tested from each tank, one from the sides of the tank halfway down the oil layer (side–centre sample) and the other from the centre of the tank, also halfway down the oil layer (centre–centre sample). At weekly intervals temperature measurements were made at both these points.

Oils Examined

Table II gives the inspection data on the oils examined. All the oils had been in storage for periods of one to five years.

TABLE II

Inspection Data of Oils in Storage

Oil	O	P	Q	R	S	T
Origin	Western Hemisphere	Middle East				
Sp gr 60°F/60° F	0·9280	0·9260	0·9185	0·9315	0·9290	0·9305
Viscosity at 122° F, Redwood No 1, sec	250	175	110	103	171	158
IP (Upper) Pour Point, ° F	25	70	45	40	5	5
Method VII, flow point, ° F	10	70	50	45	40	30
Asphaltenes, IP 6/49, wt per cent	1·6	1·2	1·0	1·1	2·1	2·3
Wax, wt per cent	9·4	11·5	9·2	9·8	7·7	7·5

Temperatures of Oils in Tanks

A summary of the results of the temperature survey is given in Table III. At the side of the tank the oils

showed, over the 18 months during which observations were made, a difference of 13·5° to 23·5° F between minimum and maximum temperatures. At the centre two of the oils showed little difference between the minimum and maximum temperatures (2° to 2·5° F), while the other two showed little difference in maximum and minimum temperatures from the corresponding side–centre position. The difference in behaviour is attributed to the tendency of oils to gel at the side of the tank, thus restricting thermal convection. The thermal insulating effect of this gel may result in the oil in the centre of a tank being quite pumpable, while if the oil had been free to cool by

TABLE III

Temperature Changes in Stored Oils from October 1955 to May 1957

Oil	Side–centre position			Centre–centre position		
	Maximum temperature, °F	Minimum temperature, ° F	Range, ° F	Maximum temperature, ° F	Minimum temperature, ° F	Range, ° F
(O) Western Hemisphere	56	41	15	52	41	11
(Q) Middle East .	58·5	55	23·5	52	50	2
(R) Middle East .	56·5	40	16·5	52	49·5	2·5
(T) Middle East .	54·5	41	13·5	54	39·5	14·5

thermal convection the whole contents of the tank might have become unpumpable.

Viscosity of the "As Received" Oil

During any period of twelve months the temperature of an oil in a storage tank, particularly when

TABLE IV

Lower and Upper Viscosities of Oils

Oil	Temp, ° F	Autumn 1955, lower viscosity, poises	Spring 1956, upper viscosity, poises	Autumn 1956, lower viscosity, poises	Spring 1957, upper viscosity, poises
(O) Western Hemisphere	50	36	48	36	60
(Q) Middle East . .	45	27	58	—	—
	50	17	31	28	—
(R) Middle East . .	45	46	65	54	70
(S) Middle East . .	45	25	51	—	56
(T) Middle East . .	50	7	8	7	—

measurements are made at the side of the tank, passes through a cycle in which the oil achieves the same temperature in two different ways; once on cooling down after the summer, and again when warming up after the winter. Table IV gives the viscosities of a number of oils determined between 1955 and 1957, when, either by cooling down or warming up, the particular oil had achieved the same temperature at different periods in the temperature cycle. The conclusion is reached that oils exhibit a lower or higher viscosity at a given temperature. The lower viscosity is attained when that temperature is reached as a result of cooling from a higher temperature: the higher viscosity at a given temperature is exhibited

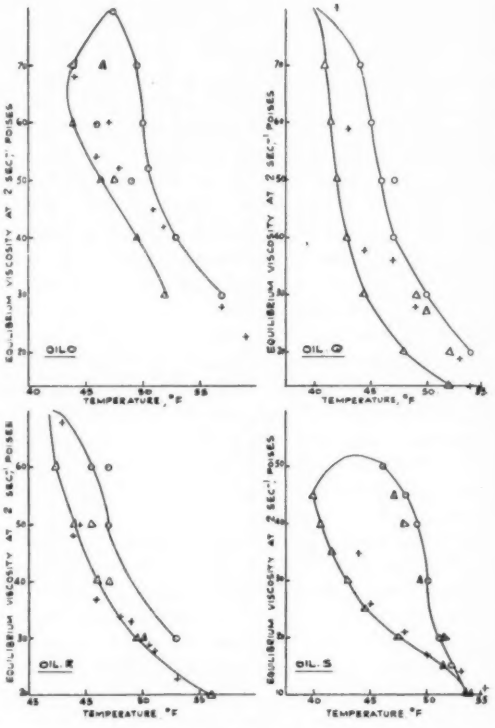

FIG 6

COMPARISON OF LOWER AND UPPER VISCOSITIES WITH VISCOSITIES AFTER METHOD XV PRETREATMENT

△—△ Lower viscosity ○—○ Upper viscosity + Method XV

when that temperature is achieved as a result of warming-up from a lower temperature. The actual value of these lower and higher viscosities appears to depend on the temperature cycle to which the oil has been subjected. Fig 6 shows the variation in the lower and higher viscosities obtained on four oils.

Viscosities of Oils after Method XV Treatment

While this work was in progress Method XV was being developed. Oils treated by Method XV invariably gave viscosities between the lower and higher "as received" viscosities (see Fig 6). It was also established that the viscosity of the Method XV heat-treated oil was independent of the condition of the "as received" sample.

Aging of Freshly-Prepared Oils

So far, work has been described on oils that have been in storage for considerable periods. Before Method XV could finally be accepted it was desirable to know how freshly-prepared oils aged and how far Method XV could be relied on to predict the extent to which the oil would age.

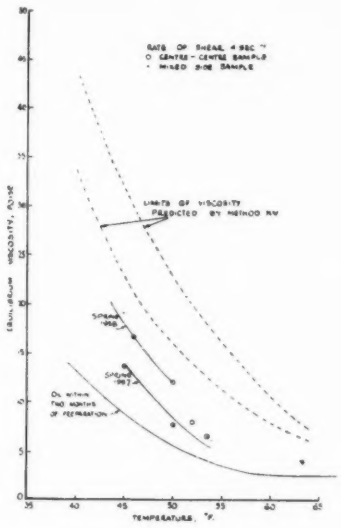

FIG 7 (*a*)

OIL U. COMPARISON OF VISCOSITY OF "AS RECEIVED" OIL WITH THAT PREDICTED BY METHOD XV

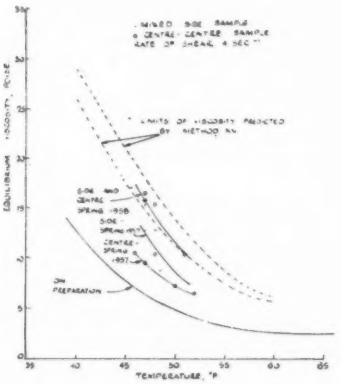

FIG 7 (*b*)

OIL V. COMPARISON OF VISCOSITY OF "AS RECEIVED" OIL WITH THAT PREDICTED BY METHOD XV

In conjunction with the British Petroleum Co and the Admiralty, the aging of an oil was followed from the day of its preparation at a refinery, through the stages of transportation to a storage depot and its subsequent behaviour in storage. The period from December 1955 to April 1958 was covered. A second oil prepared in August 1955 was examined over the period October 1956 to April 1958. The inspection data on the two oils are given in Table V. Figs 7 (*a*) and 7 (*b*) summarize the data obtained on samples taken from the side of the tanks and from the centre–centre position in the tanks and tested, after isothermal transfer, at a rate of shear of 4 sec^{-1}. At the same time as the viscosity measurements were made on the "as received" samples, the oils were also treated by Method XV, and these data are also included in Figs 7 (*a*) and 7 (*b*). After 28 months the first oil had not yet attained the viscosity level predicted by Method XV. In the case of the second oil, at the end of 35 months the "as received" viscosity was the same as that predicted by Method XV.

TABLE V

Refinery Inspection Data on the Oils U and V

Oil		U		V	
Batch weight loaded to tanker, tons		Second batch 5615	First batch 5240	First batch 5676	Second batch 5457
Sp gr 60/60° F	IP59	0·9250	0·9260	0·9245	0·9225
Flash point, ° F	IP34	214	206	235	226
Total sulphur, wt %	IP61	3·20	3·11	3·27	3·15
Viscosity at 122° F, cS	IP71	41·8	40·6	40·3	39·0
Viscosity (calc) Redwood No 1 at 122° F, sec		170	167	165	155
Flow point, ° F	Method VII	35	35	40	35
Ash, wt %	IP4	0·006	0·012	0·032	0·015
Water, vol %	IP74	Trace	Trace	Trace	Trace
Sediment, wt %	IP53	0·01	0·018	0·01	0·01
Explosiveness, %	BP240	7	7	10	10

Further work, the details of which are not presented in these figures, has shown no indication of a continued rise in viscosity of the oils with age. It therefore appears that both oils had attained their fully-aged condition in about two years. It must be appreciated, however, that the fully aged-condition of any oil is not a fixed absolute condition, as the viscosity of the oil will depend on the last seasonal temperature cycle through which the oil has passed.

From the above trials it was also established that the viscosity of an oil treated by Method XV was no higher for a partially- or fully-aged oil than for a sample of freshly-prepared oil.

ACKNOWLEDGMENTS

Part of the work described in this paper formed part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, and the paper is published by permission of the Director of the Warren Spring Laboratory. The

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APPENDIX I

FLOW POINT OF FUEL OIL USING METHOD VII

Introduction

1. (*a*) This method is used to determine the flow point of residual fuel.

(*b*) The flow point is the highest value for the pour point of the oil which can be obtained after the oil has been heat treated at different temperatures in a prescribed range.

The results of the test are intended to predict the pour point which the oil might acquire after long storage under service conditions. This value is not necessarily the same as the IP upper pour point, and often exceeds it.

Outline of Method

2. The sample is heated to 165° ± 5° F, cooled to 0° F, and then heated to and maintained at one of a series of treatment temperatures for 30 min, after which the pour point is determined by the technique described in IP 15/42. The heat treatment procedure of IP 15/42 is not employed.

The test is repeated using different treatment temperatures between 70° and 160° F until the highest value of the pour point is obtained.

Apparatus

3. (a) *Test Jar and Gasket.*—As described in IP 15/42.

(b) *Thermometers.*

(i) Pour point thermometers—conforming to the specification IP 1F.

(ii) Chilling bath thermometers—pour point thermometers are convenient for this purpose.

(iii) Other thermometers—conforming to the specification IP 3F.

(c) *Preheating Bath.*—Water bath of any convenient size and shape and equipped with means of maintaining its temperature at 165° ± 5° F.

(d) *Chilling Bath.*—Bath of any convenient size and shape and equipped with means of maintaining its temperature at −30° ± 5° F. The liquid of this bath must be fluid at −40° F.

(e) *Heat Treatment Bath.*—Water bath of any convenient size and shape equipped with means of maintaining its temperature at the required heat treatment temperatures, which lie between 70° and 160° F. This bath should be capable of maintaining any desired temperature with an accuracy of ±2° F.

(f) *Cooling Baths for Pour Point Determination.*—Fitted with jackets and disks assembled as specified in IP 15/42 for pour point determinations. The temperatures of the baths shall be 77° ± 2° F, 30° to 35° F, and lower temperatures as required by IP 15/42 for pour point determination.

Sampling and Handling Sample

4. The minimum size of laboratory sample required is one litre (2 pints), and particular care must be taken to ensure that this is fully representative of the oil under investigation. It may be necessary to warm a bulk sample in order to obtain the laboratory sample, but this warming must be so arranged that there is no possibility of heating the oil above 165° F. Likewise samples in transit must not be heated above this temperature.

> *Note:* The fact that the laboratory sample is fully representative does not eliminate the necessity for carrying out all the instructions given in the first sentence of Section 5 (*a*).

Procedure

5. (*a*) Heat the whole laboratory sample in a water bath maintained at a temperature of 165° ± 5° F until the oil temperature reaches at least 120° F. Shake the sample and pour it into the pour point test jar to a height of 2–2½ inches (51–57 mm). Close the jar with a cork carrying an IP 3 thermometer so that the thermometer bulb is immersed vertically in the sample with the beginning of the capillary ½ inch (3 mm) below the surface. Immerse the jar to a depth of 3½–4 inches (89–102 mm) in a water bath maintained at 165° ± 5° F.

(*b*) After 15 min, remove the jar from the water bath and allow it to cool in air until the IP 3 thermometer reads 130° F. At this point remove the cork and IP 3 thermometer and replace with a cork carrying an IP 1 thermometer.

(*c*) Allow the oil to continue to cool until the IP 1 thermometer reads 120° F, then plunge the jar to a depth of 3½–4 inches (89–102 mm) into a chilling bath maintained at −30° ± 5° F and allow it to stand until the oil temperature has fallen to 0° F.

(*d*) Remove the jar from the chilling bath, wipe it free from adhering cooling mixture, and immerse it to a depth of 3½–4 inches in the water bath maintained at the heat treatment temperature of 90° ± 2° F. After 30 min remove the jar, wipe all water from its surface, and determine the pour point by the technique described in IP 15/42, Section 4 (*d*) to (*h*).

(*e*) If the pour point obtained is 5° F or less, no further test need be made; if the pour point is higher than 5° F repeat the whole test twice using fresh portions of the laboratory sample but change the heat treatment of 90° F prescribed in Section 5 (*d*) to 105° F for one test and to 120° F for the other test. Immediately after heating the sample to any treatment temperature above 90° F fit the gasket on the test jar and place the jar into the jacket of a cooling bath assembled as specified in IP 15/42 for pour point determination; the bath temperature being 77° ± 2° F. When the sample has cooled to 90° F, determine the pour point by the technique described in IP 15/42 Section 4 (*d*) to (*h*), using further pour-point cooling baths at the temperatures specified in IP 15/42.

(*f*) If the value obtained for the pour point after heat treatment at 120° F is higher than after treatment at both 105° and 90° F repeat the test, following the method of paragraph 5 (*e*) but using a treatment of 140° F. If this test gives a pour point higher than the figure obtained after heat treatment at 120° F repeat the test once more, using a treatment temperature of 160° F. When these two treatment temperatures are employed use an IP 3 thermometer during the heat treatment and replace with IP 1 thermometer when the sample has cooled to 130° F.

(*g*) If the pour point obtained after heat treatment at 90° F is higher than that obtained after treatment at both 105° and 120° F repeat the test following the technique of Section 5 (*e*), but employ a treatment temperature of 80° F. Immediately after heat-treating the sample to this temperature place the test jar into the jacket of the 32° F pour point cooling bath and proceed with the pour point test without any further heating of the sample.

(*h*) If the test at 80° F then gives the highest pour point, repeat the test according to Section 5 (*g*), but use a treatment temperature of 70° F.

> NOTE: The operations described in Section 5 (*a*) to (*h*) may be performed concurrently.

(*i*) Two further tests shall be made, the heat treatment used being that previously found to give the highest pour point.

The results of these two tests, and the highest pour point previously determined, should not vary by more than 10° F. If this variation is exceeded, the whole series of tests must be repeated.

Reporting

6 (*a*) Report all values of the pour point together with the corresponding heat treatment temperatures.

(*b*) If the pour point is found to be 5° F or lower after heat treatment at 90° F, report the Flow Point as "Below 30° F."

(*c*) If two of the three results referred to in Section 5 (*i*) are identical, that figure shall be reported as the Flow Point.

(*d*) If all three results referred to in Section 5 (*i*) differ, the arithmetic mean of the three shall be reported as the Flow Point.

Precision

7. Test results for flow point should not differ from the mean by more than the following amounts:

Repeatability	*Reproducibility*
5° F	5° F

APPENDIX II

AFLAC TENTATIVE PUMPABILITY TEST FOR BOILER FUEL * (MODIFIED APRIL 1959)

Scope

1. This test is used to predict the highest viscosity at 48° F which a boiler fuel may acquire under Service conditions.

Outline of Method

2. A sample of the oil is heated in a special annular copper vessel to 165° ± 5° F and shock chilled to 32° F. It is then heated to one of the three reheat temperatures 75°, 95° or 115° F, poured into the Ferranti portable viscometer, Model VH, which is then cooled at the rate of 2° F/min to 48° F. The oil is then tested with the viscometer operating at a rate of shear of approximately 9·7 sec^{-1}.

This test is repeated using the other two reheat temperatures with the object of finding the highest viscosity at 48° F.

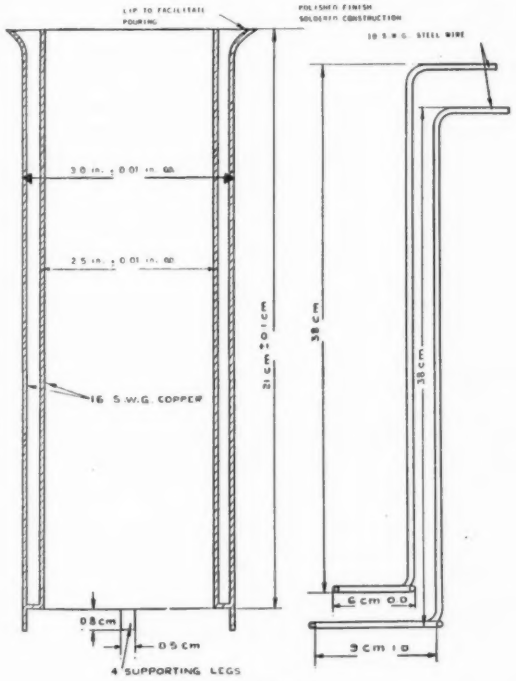

FIG A

Apparatus

3. (a) *Thermometers.*—IP 15F or ASTM 9F-53 are suitable for all operations.

(b) *Preheating Bath.*—Water bath of any convenient size and shape to accommodate the special annular copper vessel and equipped with means of maintaining its temperature at 165° ± 5° F.

(c) *Chilling Bath.*—Bath of any convenient size and shape to accommodate the special annular copper vessel, filled with a mixture of equal volumes of crushed ice and water.

(d) *Reheat Bath.*—Water bath of any convenient size and shape to accommodate the special annular copper vessel and equipped with means of maintaining its temperature at any of the required reheat temperatures of 75°, 95°, and 115° F. This bath should be capable of maintaining any desired temperature with an accuracy of ±2° F.

No	KEY ITEM
1	OUTER CYLINDER
2	INNER CYLINDER
3	GUARD RING
4	GUARD RING SUPPORT TUBE (DETACHABLE)
5	INNER CYLINDER SPINDLE
6	OUTER CYLINDER QUICK RELEASE ATTACHMENT
7	INNER CYLINDER RELEASE APERTURE
8 & 9	INNER CYLINDER QUICK RELEASE SYSTEM
10	STEADY BEARING
11	TURRET GEAR BOX
12	INNER CYLINDER LOCKING MECHANISM
13	SPRING LOADED SECONDARY BEARING
14	SYNCHRONOUS MOTOR
15	PHASING CONDENSER
16	TRANSFORMER
17	MAIN JEWELLED BEARING
18	TORQUE SPRING
19	MAX. INDICATING FRICTION POINTER
20	VISCOSITY INDICATING POINTER

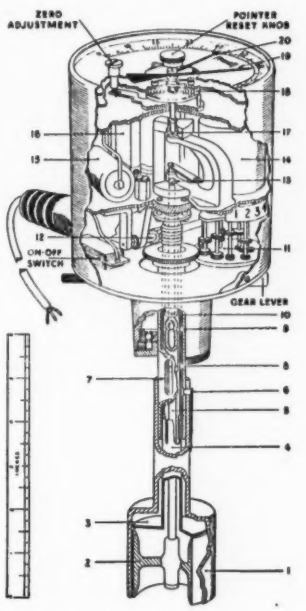

FIG B

(e) *Stopwatch.*—Stopwatch graduated in ½ sec.

(f) *Special Annular Copper Vessel.*—Special annular vessel made of 16 swg copper as in Fig A (capacity approximately 165 ml). The outer cylinder is 3·00 ± 0·01 inch OD; the inner cylinder is 2·50 ± 0·01 inch OD, thus the width of the annulus is 0·186 ± 0·015 inch. The height of the container is 8·25 ± 0·01 inch. The annular vessel shall be provided with two ring stirrers made of $\frac{1}{16}$-inch wire as shown in Fig C, the larger stirrer fitting round the outside of the annular copper vessel and the smaller stirrer fitting in the centre.

(g) *Oil Container for Viscosity Determinations.*—A special vessel made of ⅛-inch duralumin to the dimensions given in Fig B. The vessel is a sliding fit on the VM outer cylinder of the Ferranti viscometer. The height of the vessel without cap is 3·5 ± 0·1 inch. The cap to hold the viscometer cylinder in position has a knurled top and bayonet fitting. The vessel has four grooves in the side to allow easy flow of oil past the viscometer cylinder.

(h) *Viscometer Bath for Oil Container.*—Bath of any convenient size and shape filled with water such that the oil container (*g*) can be immersed in it and the Ferranti viscometer (*i*) can be placed in position in the oil in the container. The bath shall be capable of being maintained at temperatures of 75°, 95°, and 115° F, all ±2° F. This bath must be capable of being cooled at the rate of 2° F/min, and of being maintained at a temperature of 48° ± 0·25° F.

NOTE: It has been found that a controlled rate of cooling of 2° F/min is easily obtained by the addition of small lumps of ice at the requisite intervals.

* Sometimes known as Method XV.

(i) *Ferranti Co-axial Cylinder Viscometer.*—A Ferranti 3-speed portable viscometer Model VH fitted with a Tufnol shaft and with a 20-g cm spring VM outer cylinder and B inner cylinder (Fig D).

Four $\frac{1}{16}$-inch dia holes are drilled symmetrically into the top of the VM outer cylinder and guard ring, as shown in Fig D, to allow oil to flow easily into the gap between the cylinders.

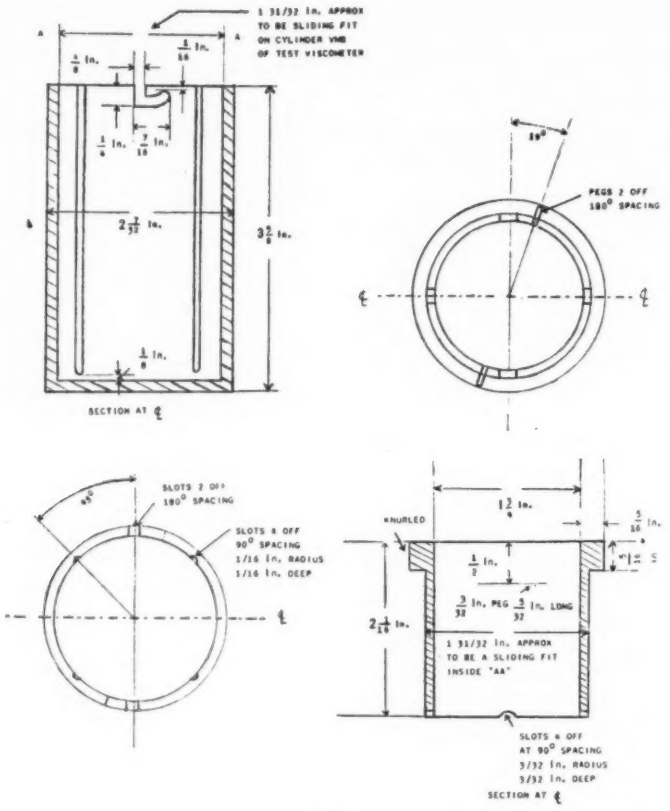
1 31/32 In. APPROX TO BE SLIDING FIT ON CYLINDER VMB OF TEST VISCOMETER
SECTION AT ℄
PEGS 2 OFF 180° SPACING
SLOTS 2 OFF 180° SPACING
SLOTS 4 OFF 90° SPACING 1/16 In. RADIUS 1/16 In. DEEP
KNURLED
1 31/32 In. APPROX TO BE A SLIDING FIT INSIDE "AA"
SLOTS 4 OFF AT 90° SPACING 3/32 In. RADIUS 3/32 In. DEEP
SECTION AT ℄

FIG C

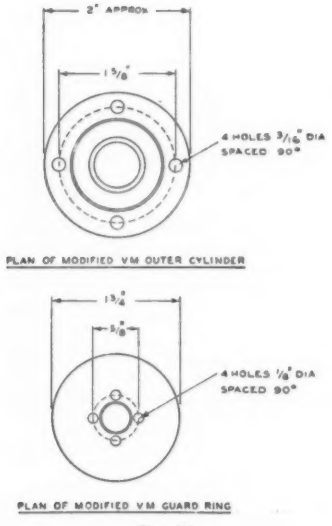

FIG D

Sampling and Handling Sample

4. The minimum quantity of oil required for the complete test is about 800 ml. Particular care must be taken to ensure that this is fully representative of the bulk sample. To obtain this test sample, warm the bulk sample to at least 120° F, taking care not to heat any part of it to above 165° F. Shake the bulk sample and fill any suitable container.

Measurement of Viscosity at 48° F with the Ferranti Portable Viscometer

5. (*a*) Fit the oil container on to the viscometer and place the assembly in its working position in the viscometer bath. Maintain this bath at the reheat temperature of 75° F.

(*b*) Heat the laboratory sample in a water bath maintained at a temperature of 165° ± 5° F until the oil temperature reaches at least 120° F. Shake the sample and pour it into the special copper vessel to within about 1 inch of its top. Immerse this copper vessel, to within 1 inch from the top of the vessel, in the preheating bath maintained at 165° ± 5° F and fit the two ring stirrers.

(*c*) After 10 min remove the copper vessel with the ring stirrers from the preheating bath and plunge *immediately* into a chilling bath containing a mixture of equal volumes of crushed ice and water. Keep the copper vessel in the chilling bath for 5 min ± 10 sec and during this time operate the stirrers at the rate of at least one double stroke per second.

(*d*) Remove the copper vessel from the chilling bath and immerse it, to within 1 inch of its top, in the reheat bath

maintained at 75° ± 2° F. Maintain at this temperature for 10 min.

(*e*) With the viscometer and container assembled as in Section 5 (*a*), transfer sufficient oil to cover the top of the outer cylinder to a depth of 1 inch.

(*f*) Maintain the viscometer bath at 75° ± 2° F for 20 min and then cool at the rate of 2° F/min until the temperature reaches 48° F. Maintain at 48° ± 0·25° F for 20 min.

(*g*) At the end of 20 min start the viscometer with the gear change lever set to speed 3. Make observations of the instrument reading at 10 and 20 min. Throughout this test period the viscometer bath must be maintained at 48° ± 0·25° F. Convert the scale readings to apparent viscosity in poise by multiplying by the appropriate factor.

(*h*) Repeat the whole test using reheat temperatures of 95° and 115° F.

Reporting

6. (*a*) Report the viscosities measured in the Ferranti viscometer at 10 and 29 min for reheat temperatures of 75°, 95°, and 115° F.

(*b*) Report the highest viscosity after 20 min as the Pumpability Viscosity in Poise.

(*c*) Report the reheat temperature which gave the pumpability viscosity.

Timetable for Test

Operation	Time minutes
Heating laboratory samples to 120° F, shake and pour into special copper vessel and immerse in bath at 165° F: Set up viscometer in bath at reheat temperature	Approx 15
Time in preheating bath	10
Transfer to chilling bath and fit two ring stirrers	Less than 1
Time in chilling bath	5
Transfer to reheat bath	Less than 1
Time in reheat bath	10
Transfer to oil container	Approx. 2
Time in oil container before cooling	20
Time of cooling for:	
Reheat 75° F	13·5
Reheat 95° F	23·5
Reheat 115° F	33·5
Time at 48° F	20
Time for viscosity measurements	20
Time of complete test for:	
Reheat 75° F	Approx 2 hr
Reheat 95° F	Approx 2 hr 10 min
Reheat 115° F	Approx 2 hr 20 min

THE YIELD VALUE OF ADMIRALTY FUEL OIL*

By R. J. RUSSELL† (Fellow)

THE SELECTION OF A TEST METHOD TO REPLACE THE POUR POINT METHOD

If a fuel oil has been cooled to a temperature at which it gels it still may be made to flow in a pipeline by applying a sufficiently high pressure differential. Thus the pour point of an oil does not give the minimum temperature at which it can be handled. However, at temperatures below the pour point flow can be obtained only by using suitable handling equipment. To decide on the handling equipment, tests are required which indicate:

(1) Whether it is possible to start flow.

(2) The rate of flow once movement has started.

Once the conditions for starting flow have been established, it is necessary to investigate how flow rates change with change of handling conditions. Such an investigation will show whether additional handling facilities are necessary to ensure adequate flow rates.

Both the initial movement and the subsequent flow of oil in a pipe are caused by the application of shearing stress. It is possible to characterize the shear conditions in a pipe in terms of the average shearing stress at the pipe wall. This is given by the formula:

$$S = \frac{RP}{2L} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where S = average shearing stress at the pipe wall;
R = radius of the pipe;
P = pressure differential along it;
L = length of the pipe.

During the initial movement of gelled oil in a pipe the flow rate obtained is of secondary importance. Also the formula (1) above indicates that the shearing conditions may vary considerably from pipeline to pipeline. Thus a test to predict the practical start-up performance of a fuel oil when in the gelled condition should primarily operate under defined shearing stress conditions. If the method is to be suitable for use as a specification fuel oil test it should also be relatively short and simple.

The pour point procedure has long been known [1] to be unsatisfactory for predicting the low temperature flow properties of fuel oils in installations. It has the disadvantage that it operates under an undefined shearing stress and therefore cannot be related to any particular practical pumping condition.

Any test procedure to replace pour point should correlate better with practice. As indicated above, a prime requirement was that it should operate under defined shearing stress conditions. The simplest test meeting this requirement appeared to be one which measured the shearing stress which was just sufficient to start the flow of a gelled fuel oil. This shearing stress was called the "yield value" of the oil. The most promising method to measure the yield value in

* MS received 29 October 1959.

† The British Petroleum Co. Ltd.

a way which predicted full-scale performance was to make tests in the laboratory in a scaled-down pipeline. This could conveniently be done by testing the oil in a U-tube.

At the time Admiralty Fuels and Lubricants Advisory Committee's work on yield values was started,

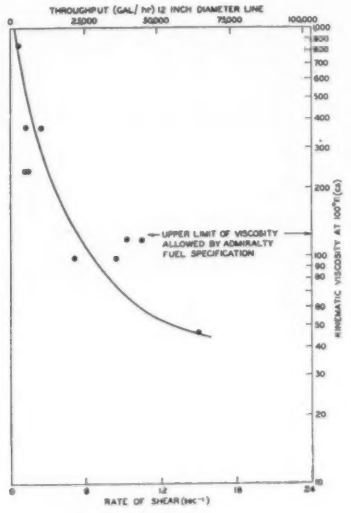

FIG 1

EFFECT OF VISCOSITY AT 100° F ON THE RATE OF SHEAR AT WHICH THE STEADY SHEARING STRESS EQUALS THE YIELD VALUE

laboratory experiments [1] had shown that even in a laboratory yield value U-tube of relatively small dimensions the phenomenon of yielding of a gelled oil was not simple. It had been shown that the shearing stress which caused yielding of a fuel oil varied with the length of the test U-tube. It had also been shown that when a U-tube containing gelled oil was cooled further, sub-atmospheric pressures were developed near the mid-point of the tube. During cooling, movement of the gel had been found to occur, a phenomenon which probably caused weakening of the gel, which was subsequently tested. Therefore, although the yield value test method discussed in this paper is the one that would be expected to relate to practical performance in the most direct manner, it does not measure an absolute property of the fuel. It is possible to visualize methods which would measure the absolute shearing stress which would cause an elementary volume of a gel oil to yield. The use of such methods to predict field performance would inevitably involve a large correlation programme between test results and field performance. To avoid such a programme, the AFLAC work was entirely devoted to measurement of yield values in U-tubes. No other method was given serious consideration.

CONDITIONS UNDER WHICH MEASUREMENT OF YIELD VALUE IS IMPORTANT

Once flow has been started in any practical installation, it is normally essential not only to move the oil but also to move it at an economic rate. This means that the viscosity of the oil under the yield value shearing stress must be reasonably low. At the time the AFLAC work was started the general behaviour of fuel oils below their pour point had been investigated in the laboratory. Testing a number of oils for yield value in a U-tube and for viscosity in a coaxial cylinder viscometer had shown that when the oils were 10° F or more below their pour point that rate of shear at the yield value shearing stress correlated with the kinematic viscosity at 100° F. With Admiralty grade fuel oils this yield stress was sufficient to give a high rate of shear once the oil had been broken down by the shearing. This is illustrated in Fig 1. The Admiralty's stated requirement was that pumpability was required at 32° F. Thus, except in special cases

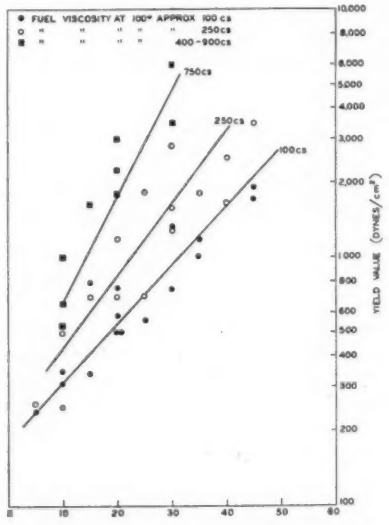

FIG 2

EFFECT OF TEMPERATURE BELOW POUR POINT AND VISCOSITY AT 100° F ON YIELD VALUE

where the pour point of the oil was close to, or less than, 32° F, the yield value appeared to be the controlling factor for flow of Admiralty fuel oil.

CORRELATION OF YIELD VALUE WITH POUR POINT

Figs 2 and 3 show the results of tests made on fuel oils in which both pour point and yield value were measured after the same heat treatment procedure. They show that there is a general relationship between

TABLE I

Effect of Wall Material of U-tube on Yield Value
(Oil Pretreated in U-tube by Method VII)

Oil viscosity at 100° F cS	Heat treatment temperature, ° F	Pour point after heat treatment, ° F	Yield value (dynes/cm²) at 32° F in			
			Smooth bore glass U-tube	Roughened bore glass U-tube	Stainless steel steel U-tube	Composite * glass/stainless steel U-tube (stainless steel) (bore)
85·7	80	35	250, 240 140, 250	200, 360 430, 390	—	—
85·7	90	30	300, 300 310, 240	430, 460 370, 260 300	490, >510 610, 560	450, 250
85·7	105	25	200, 240	330	—	360, 210 180
97·7	90	45	670, 670 670	780, 890 780	1220, 1170 1280, 1670 1140, 1210	870, 670 960, 740 780

* These figures are lower than those found with the stainless steel tubes because of the reduced thermal shock during heat treatment.

yield value and pour point, the yield value increasing as the difference between test temperature and pour point increases. However, it is also evident that for any particular difference between the temperature at which the yield value was measured and the pour point, oils of higher viscosities at 100° F have higher yield values. In addition, there is a fair scatter in the relationship between yield value, pour point, and viscosity; thus the yield value of an oil cannot be predicted with certainty from its pour point and viscosity at 100° F.

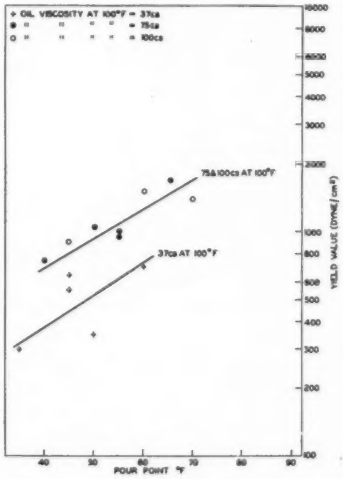

FIG 3

EFFECT OF CHANGE IN POUR POINT ON YIELD VALUE AT 32° F
(Oil preheated by Method VII)

Admiralty requirements differ from those of ordinary commercial practice, since flow has to be guaranteed after the fuel has been stored for an indefinite period of years. AFLAC work had shown that the IP upper pour point test was unsuitable for this purpose. Therefore AFLAC had first developed for this purpose a special heat treatment procedure based on pour point measurement (the Method VII Flow Point Test*).[2] To make the results of the Method VII test procedure bear a closer relationship to the expected fuel oil performance, different maximum flow points were introduced into the specification for oils of different viscosities at 122° F. It is clear that the use of such a method to control the low temperature flow properties of the fuel oil can at best be only approximate, since it makes no allowance for differences between the yield value/pour point relationship that might be found with fuels of different compositions or from different crudes. The use of two tests to predict the performance of a material in a way which is not directly controlled by either of them is always open to objection. Therefore it was decided that AFLAC Panel F should investigate fully the possibility of developing a direct measurement of yield value at 32° F. It was early apparent in this work that the yield value test did not have a very high intrinsic accuracy. Large variations of the type shown in Table I were found. However, the repeatability of the yield values test cannot be directly related to that of the pour point test. Figs 2 and 3

* The AFLAC Method VII heat treatment procedure has four stages: (1) preheating the oil to 165° F for half an hour (to render freshly-blended oils susceptible to subsequent treatment); (2) chilling to −30° F for 10 minutes in a pour point tube (to enable the optimum structure to be formed in later heating and cooling); (3) reheating for half an hour in the pour point tube to an optimum temperature for developing structure on subsequent cooling; (4) cooling and measuring the pour point of the treated oil.

show that a change in pour point of 10° F is equivalent to a change in yield value at a constant temperature of from 50 to 160 per cent. Experimentally it was found that repeat pour points were more likely to differ by 10° F than repeat yield values by 100 per cent.

CORRELATION OF YIELD VALUE WITH PRACTICAL PERFORMANCE

The early work on the yield value test showed that very large variations in the yield value resulted from variations of heat treatment procedure. Therefore, data were required to show how the various heat treatments predicted the results found in practice. Since at that time there were no full-scale data available on the pumping behaviour of fuel oils, simulated full-scale data had to be obtained on laboratory samples. This was done by loading samples into yield value U-tubes at laboratory temperature, cooling directly to 32° F, and measuring yield values (these are called " as received " yield values).

As discussed in another paper,[3] warming samples from tank to normal laboratory temperatures affects their viscosity on re-cooling to the tank temperature. It is therefore possible that the " as received " yield values so measured were not the same as would have been obtained on oil in a tank at 32° F.

However, to obtain the best " as received " values possible, special samples of the fuel oils were taken from Admiralty tanks. These samples were subjected to the minimum possible heating between sampling and testing. The sample temperature at the testing laboratory was always above the pour point. Therefore, when testing the oils, their structures were reformed in the U-tubes during cooling, thus avoiding effects due to shearing. The procedure gave the best estimates that could then be made of fuel oil yield values at 32° F. All the fuel oils tested in the work had been stored for several years, and the measured yield values therefore indicate the probable yield values of stored oils at 32° F. These measured yield values formed reference values with which the results measured after using heat treatment procedures were compared. The aim was to adjust the heat treatment procedures so that the results after heat treatment were slightly higher than the results on the " as received " samples. This would automatically provide a margin of safety.

THE CO-OPERATIVE DEVELOPMENT OF THE YIELD VALUE TEST

The work of AFLAC Panel F on the yield value test involved, in all, between 1000 and 2000 yield value tests. It can be considered under two main headings:

(*a*) The development of heat treatments which were applicable to the widest range of fuel oils.

(*b*) The effects of apparatus variables and the precision of results.

(a) *Heat Treatment Procedure*

The Admiralty specification test method [2] had been developed mainly on Middle East oils. With these oils the procedure gave flow points which were very close to the pour points of fuel oil blends to the same specifications which had been tested without heat treatment after installation aging. However, when certain fuel oils obtained from Curacao were tested, the pour points determined on aged oils without heat treatment were much higher than the flow points determined following Method VII heat treatment.

Work was therefore done at the Fuel Research Station to develop a heat treatment procedure which increased the flow points of these Curacao oils. It

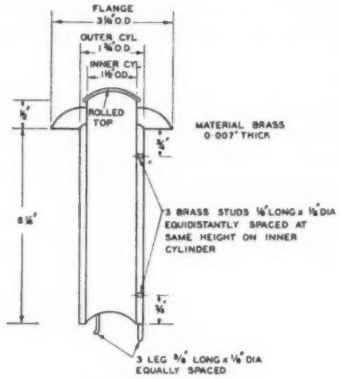

FIG 4

SECTIONAL VIEW OF HEAT TREATMENT VESSEL

was found that this result could be achieved by modifying the shock chilling stage of the Method VII heat treatment procedure. The modifications necessary were:

(i) To increase the rate of cooling. This was done by using the annular heat treatment container shown in Fig 4 in place of the pour point tube of Method VII.

(ii) To change the temperature to which the oil was shock chilled from −30° to 0° F.

This was to ensure that when testing Middle East oils the same pour point was obtained as had been previously obtained by Method VII.

The modified method was called Method XI.

As discussed below, when making yield value tests in U-tubes it was desirable to shock chill the oil in the test U-tube. This introduced no new shock chilling requirement. However, the manipulation of the samples in the shock-chilling bath had to be adjusted to allow for the differences between the U-tube and the shock-chilling apparatus of Fig 4. To distinguish it from the method developed for shock chilling in pour

point tubes the U-tube heat treatment method was called Method XIII. It appeared equal to the Method XI test in the range of applicability to different oils.

(b) *Effect of Test Variables*

(i) *The Length/Diameter Ratio of the U-tube.* Earlier work had established the importance of length/diameter ratio, and the conclusion had been reached that relatively high ratios of length/diameter were necessary to obtain results. In most ships the length/diameter ratio of the suction pipes varied in value but had a maximum of about 400. Therefore, since the test U-tube could be considered as a small-scale suction pipe, it was decided that a length/diameter ratio of 300 would be suitable. This length/diameter ratio has the advantage that it is in the range which the earlier work had indicated would not affect the determined yield value.

(ii) *Rate of Application of Pressure.* Some tests were made to investigate this variable, but they indicated that the rate of application of pressure had only a minor effect on yield value. The yield value was therefore measured by increasing the applied pressure to the U-tube in increments of 0·5 psi. This increment was equivalent to an increment of 30 dynes in the yield value. Similarly, the time at each pressure value was found to be relatively unimportant, and this was therefore standardized at 5 minutes, a time which gave ample opportunity for the oil to move and which kept the total time of the test within practical limits.

TABLE II

Effect of Rate of Cooling on Measured Yield Values

(a)—*Oil Cooled after Four Years Storage in an Installation Tank*

Oil characteristics—Kinematic viscosity at 100° F = 76·9 cS
IP upper pour point = 65° F

Laboratory	Yield value (dynes/cm²) at 32° F after				
	Shock cooling to 32° F	Cooling to 32° F over 1 hr	Cooling to 32° F over 2 hr	Cooling to 32° F over 4 hr	Cooling to 32° F over 6 hr
1	1500	750	690	650	—
2	1480	—	650	730	900
3	—	1010	930	730	—
4	1320	620	490	500	—

(b)—*Oil after Shock Cooling followed by Heat Treatment at 105° F*

Method of cooling	Yield value (dynes/cm²) at 32° F of	
	Old kinematic viscosity at = 97 cS 100° F IP (upper) pour point ° F = 40° F	Oil kinematic viscosity at = 81 cS 100° F IP (upper) pour point = 45° F
Shock chill to 32° F from 105° F	1940, >1400	—
Cool in pour point tube to 70° F, fill into U-tube and then:		
(i) Shock chill to 32° F	800, 830, 840 750, 820, 820	170, 190 160, 170
(ii) Cool to 32° F in 20 min.	420, 440 320, 380	—
(iii) Cool to 32° F in 40 min.	210, 160 250, 250	— 240, 270

(iii) *Tube Material.* The measured yield value depends on the material of the tube in which it is determined. When in the same rheological condition an oil will have a higher apparent yield value in a tube with a rougher surface (see Table I). In the early tests glass capillary tubes were used. These were satisfactory, but it was felt that since the object of the test was to simulate practice, it would be preferable to change to a rougher surface. Therefore, it was decided to standardize on stainless steel U-tubes and higher yield values were in fact measured when these U-tubes were adopted.

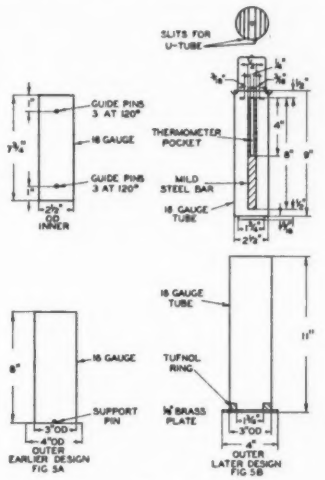

FIG 5

SECTIONS OF U-TUBE COOLING UNITS

(iv) *The Effect of Rate of Cooling of the U-tube to the Test Temperature.* Tests were made to investigate how variations in cooling rate would affect yield values. Table II shows that if the U-tubes are shock chilled to the test temperature considerable increases in measured yield value are obtained. This is especially so if the starting temperature from which the U-tube is shock chilled is high. Table II also shows that variation of rate of cooling over the cooling rates most easily obtained in laboratory apparatus has little effect.

However, it was considered desirable to standardize on cooling rate, and for this purpose the apparatus shown in Fig 5 (*a*) was designed to control the cooling rate. To do this the inner vessel was filled with *iso*-propyl alcohol and then placed in the outer vessel. The whole unit was then cooled in a bath maintained at a constant temperature (20° F to cool the inner container to 32° F in about two hours). In tests with this unit it was found that the temperature was higher near the top of the inner container. Hence, when transferring the U-tube from the cooling unit to a

constant temperature test bath the U-tube suffered some thermal shock. To overcome this the cooling apparatus was modified as shown in Fig 5 (*b*). This unit obtained temperature equalization by means of the heavy mild steel bar which extended from the top to the bottom of the inner container. The U-tubes rested against this steel bar and so remained at an even temperature throughout the cooling. The controlled rate of cooling was again obtained by placing the inner container, containing *iso*propyl alcohol, in the outer container and immersing the whole assembly in a constant temperature bath at 20° F.

TABLE III

Comparative Tests Including and Omitting Indicator Tubes

Pre-treatment Method XI—cooled to 32° F in 2 hours

Preheating temperature, ° F	Reheating temperature, ° F	Yield value (dynes/cm²) at 32° F	
		Measured using indicator	Measured omitting indicator
155	70	600	580
	80	260, 220	270, 200
	90	100, 60	120, 60
	105	30, 30, 30	30
175	70	410, 320	320, 350
	80	260, 260, 210	200
	90	160, 100	130, 100
	105	80, 100, 100	80

(v) *Indication of Yield of the Oil.* It was first thought that an accurate measure of the movement of the oil was necessary, and an indicator of the type shown in Fig 6 (*a*) was used for this purpose. Temperature fluctuations in the air over the test bath were found to cause movement of the alcohol in the indicator tube without yielding having occurred. To obviate spurious results due to this cause, the indicator shown in Fig 6 (*b*) was designed. This indicator had far less air space between the oil surface and the alcohol pellet. However, when it was used, small random movements of the indicator were still observed and the indicator assembly was further modified by filling up the central nipple to reduce the dead space still further.

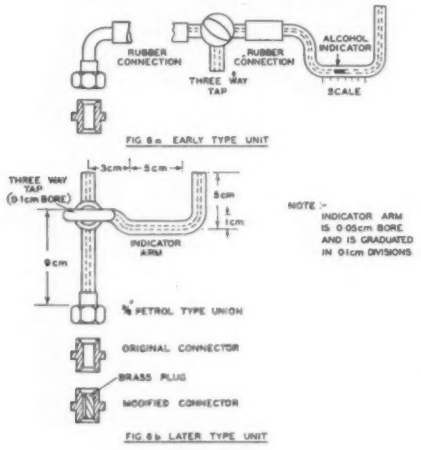

FIG 6

INDICATOR UNITS

It was then questioned whether the indicator gave a better indication of movement of the oil than was obtained by visual observation of the free surface. A series of tests were therefore made, and the results, given in Table III, showed that the omission of an indicator had no significant effect on the results. It was therefore decided to omit indicators in the later

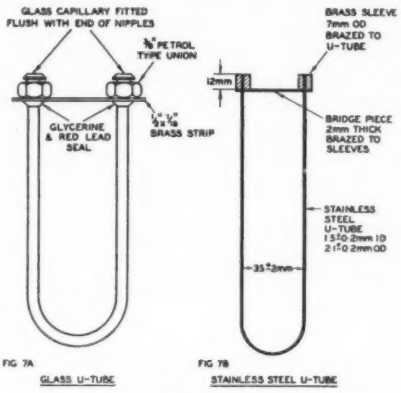
GLASS CAPILLARY FITTED FLUSH WITH END OF NIPPLES
⅜" PETROL TYPE UNION
GLYCERINE & RED LEAD SEAL
¼" x ⅛" BRASS STRIP
12mm
BRASS SLEEVE 7mm OD BRAZED TO U-TUBE
BRIDGE PIECE 2mm THICK BRAZED TO SLEEVES
STAINLESS STEEL U-TUBE 1·5 I·D 2mm O·D 2·5 I·D 2mm O·D
35±2mm
FIG 7A
GLASS U-TUBE
FIG 7B
STAINLESS STEEL U-TUBE

FIG 7

CONSTRUCTION OF U-TUBES

TABLE IV

Co-operative Tests at 32° F in Glass Tubes

(a) *On Samples Cooled without Heat Treatment*
(b) *On Samples Heat Treated by Aging Procedures Method VII and Method XI*

Oil properties		Laboratory	Yield value at 32° F (dynes/cm²)		
IP (upper) pour point, ° F	Kinematic viscosity at 100° F, cS		On untreated samples cooled to 32° F in 2 hr	On samples heat treated by Method VII and shock chilled to 32° F	On samples heat treated by Method XI and cooled to 32° F in 2 hr
40	41·6	1	130	540	370
		2	130	480	350
		3	170	520	510
		4	100	480	110
		5	160	670	140
		6	220	530	450
65	76·9	1	880	>1700	1240
		2	700	>2500	1540
		3	760	2540	2240
		4	540	2070	1190
		5	—	—	1820
15 *	96·6	1	140	470	410
		2	340	370	440
		3	420	460	540
		4	220	320	110
		5	650	330	—
		6	—	440	660

* Oil from Curacao.

tests and to observe yielding by direct observation on the exposed surface of the oil. To facilitate such observation the U-tubes were redesigned as shown in Fig 7 (*b*).

The investigations into apparatus variables described above were made at various times by Panel F of AFLAC, and the general conclusion was that, providing the procedures and apparatus used were relatively well standardized, minor changes in procedure or apparatus would have little effect.

However, when co-operative tests were made to determine the yield value of fuel oils by Method VII (shock chilling the oil to 32° F before testing) and by Method XI (cooling the oil to 32° F in about 2 hours), it was found that the reproducibility, especially of Method XI, left much to be desired. A comparison of the results is given in Tables IV and V. The results given in Table IV onwards are normally the results of four tests at each of a number of different heat treatment temperatures. Where no reheat temperature is given the result reported is that for the reheat temperature which gave the highest yield values.

Tables IV and V show that, in addition to being less reproducible, the Method XI test method in general gave lower results than the Method VII test. They

TABLE V

Average Yield Values Measured in Co-operative Tests

(a) *On Samples Cooled from Laboratory Temperature to 32° F*
(b) *On Samples Heat Treated by Aging Procedures Method VII and Method XI*

Fuel properties		Average yield value on untreated sample after cooling to 32° F in 2 hr	Average yield value at 32° F after treatment by	
IP (upper) pour point, ° F	Kinematic viscosity, at 100° F, cS		Method VII shock chilled to 32° F	Method XI cooled to 32° F in 2 hr
65	76·9	700	2460	1670
15 *	96·6	380	390	510
40	97·7	500	690	—
15	101	150	240	—
15	107·5	70	180	—
40	41·6	150	540	390

* Oil from Curacao.

also show that Method VII rated the Curacao oils at about their expected performance. However, it was considered that for a heat treatment procedure to be reliable the yield value obtained should be comparable with the " as received " yield value after the same rate of cooling as used on the " as received " sample. Therefore, it was considered that the Method VII procedure was not fully acceptable, and work was carried out to find where the causes of the poor reproducibility of the Method XI test lay.

The pre-heating temperature used was first investigated, but it was shown that close control of this variable did not greatly improve the reproducibility of the test (Table VI (*a*)). It was also shown that changing the pre-heating temperature over the range 155° to 212° F did not significantly affect the results obtained in the test (Table VI (*b*)).

Method VII and Method XI differ mainly in the thermal shock used after the pre-heating stage. Therefore insufficient control of the thermal shock applied in Method XI was suspected as being the cause of its poor reproducibility.

It was also considered that the reproducibility of the test might be improved if the heat treatment of the sample was done in the U-tube. Pouring from

TABLE VI

Effect of Preheating Temperature on Yield Value

(a). *Effect of Close Control of Preheating Temperature (to 165° ± 1° F)*

Laboratory	Yield value (dynes/cm²) at 32° F of			
	Oil kinematic viscosity at 100° F = 81·9 cS IP upper pour point = 30° F		Oil kinematic viscosity at 100° F = 60·0 cS IP upper pour point = 10° F	
	Heat treated Method VII and then shock chilled to 32° F	Heat treated Method XI and then cooled to 32° F over 2 hr	Heat treated Method VII and then shock chilled to 32° F	Heat treated Method IX and then cooled to 32° F over 2 hr
1	260	410	100	220
2	180	460	125	260
3	350	—	90	260
4	250	230	90	170
6	270	—	100	—

(b). *Effect of Varying Pretreatment Temperature over Range 155°—212° F on Yield Value by Method XI Followed by Cooling to 32° F in 2 Hours*

Laboratory	Yield value at 32° F							
	Oil kinematic viscosity at 100° F = 96·6 cS IP upper pour point = 20° F				Oil kinematic viscosity at 100° F = 41·6 cS IP upper pour point = 40° F			
	Preheat temperature, ° F				Preheat temperature ° F			
	155	165	175	212	155	165	175	212
1	590	410	350	—	330	370	430	—
2	—	—	—	—	410	340	480	—
4	310	270	190	470	430	420	850	590
5	540	500	140	—	—	—	—	—
6	650	650	660	—	—	—	—	—

the heat treatment can into the test U-tube was considered to be undesirable because:

(i) Structure present in the oil might be destroyed during the transfer.

(ii) The oil could cool to an unknown extent during the transfer.

(iii) The small U-tube sample might not be fully representative of the sample in the heat treatment can.

The alternative procedure of heat treating the sample in the test U-tube was therefore investigated. Due to their different dimensions, the special heat treatment can and the U-tube were expected to cool at different rates during the shock-chilling stage of the treatment. Therefore it was to be expected that different yield values would be measured on samples on which the heat treatment was carried out in the

special can and those on which it was carried out in the U-tube. This was in fact found, as is shown in Table I.

Tests to find out how to standardize these shock-chilling procedures showed (Table VII) that the shock chilling was critical and had its greatest effect over the temperature range between 120° and about 60° F.

TABLE VII

Effect of Shock Cooling Conditions on Yield Value at 32° F

Oil

Kinematic viscosity at 100° F = 96·6
IP (upper) pour point = 20° F

Oil Preheated in Metal U-tube

30 min at 165° F, cooled to 32° F as specified below, stored at 32° F for 10 min and finally heat treated at 70° F

Cooling conditions	Yield value at 32° F, dynes/cm²
Transfer to ice bath within 3 sec	1800
Cool in air 1 min, transfer to ice bath	940
,, ,, 3 ,, ,, ,,	210
,, ,, 5 ,, ,, ,,	120
,, ,, 10 ,, ,, ,,	190
,, ,, 30 ,, ,, ,,	160
Transfer to bath at 120° F within 3 sec Store 10 min, transfer to ice bath within 3 sec	1150
Transfer to bath at 70° F within 3 sec Store 10 min, transfer to ice bath within 3 sec	320

Delay in transferring the shock-chilling container from the pre-heating bath to the shock-chilling bath gave lower results. Such low results had been reported by

particular attention was paid to the immediate transfer of the test U-tube from the pre-heating bath to the shock-chilling bath. The results obtained showed slightly better reproducibility, but were not fully satisfactory. It also appeared that a shock-chilling

TABLE IX

Tests to Establish Shock Chilling Variables in Method XIII

Properties of Oil Tested—Kinematic Viscosity at 100° F = 43·3 cS, IP (Upper) Pour Point = 25° F

Reheat temperature, ° F	Shock-chilling temperature, ° F	Stirring used on shock-chilling bath	Yield value (dynes/cm²) at 32° F with shock-chilling bath liquid		
			*iso*Propyl alcohol	White spirit	Water
80	60	Nil	110	—	350
		Paddle	—	90	—
		Pump	—	—	350
	50	Nil	260	—	870
		Paddle	—	350	—
	40	Nil	380	490	1070
		Pump	—	640	1190
90	60	Nil	190	—	350
		Paddle	—	200	—
		Pump	—	—	460
	50	Nil	320	—	—
		Paddle	—	410	—
		Pump	—	550	—
	40	Nil	380	460	1420
		Pump	—	810	1440
105	60	Nil	220	230	470
		Paddle	—	200	—
		Pump	—	370	520
	50	Nil	260	430	580
		Paddle	—	380	—
		Pump	—	520	630
	40	Nil	350	520	670
		Pump	—	550	—

Note: Shock-chilling bath for no stirring and pump stirring is the inner container shown in Fig 6 (*b*).

Paddle stirring is in large bath.

TABLE VIII

Co-operative Tests using Shock Chilling in U-tube

Inspection data on oil		Heat treatment procedure	Temperature of shock chilling bath, ° F	Yield value at 32° F measured in laboratory				
Kinematic viscosity at 100° F, cS	IP (upper) pour point, ° F			1	2	4	5	6
96·6	20·0	No Treatment	—	590	—	—	—	—
		Method XIII	40	1070	1160	490	—	920
			50	710	660	670	—	490
			60	220	280	150	—	260
—	—	No Treatment	—	—	—	—	—	—
		Method XIII	40	280	630	160	550	350
			50	260	350	130	350	200
			60	120	120	110	150	90
41·6	40	No Treatment	—	230	360	280	180	320
		Method XIII	40	560	—	400	920	920
			50	810	770	490	700	660
			60	350	380	380	350	290
			40 *	400	—	780	880	—
			50 *	780	720	690	710	—
			60 *	460	410	250	400	—

* Repeat series of tests.

one or two laboratories in the earlier co-operative tests. In view of this, further co-operative tests were undertaken (Table VIII) in which shock chilling temperatures of 40°, 50°, and 60° F were used. In these tests temperature of 50° F apparently gave yield values which were in best agreement with the " as received " figures determined on the oils.

It was found in discussion that the different labora-

tories were using different liquids for shock chilling the U-tubes. An investigation showed (Table IX) that both change of liquid and difference in liquid stirring in the shock-chilling bath had a considerable effect on the results. Three liquids were tried, and of these *iso*propyl alcohol gave the lowest results, white spirit the next, and water the highest. Increasing the stirring increased the yield value subsequently measured.

A study of the figures obtained in conjunction with the " as received " yield values of the oil suggested that using *iso*propyl alcohol as the shock-chilling liquid and a shock-chilling bath temperature of 50° F would probably give a satisfactory result. One reason for choosing *iso*propyl alcohol was that it is a pure compound, and therefore reproducible. It was also decided that it would be better not to stir the shock-chilling bath, thus eliminating possible differences in stirring between laboratories. To ensure that convection had the same effect in all tests it was decided to use the inner container of the cooling unit shown in Fig 5 (*b*) as the shock-chilling unit.

A further co-operative programme was therefore undertaken using this much more elaborate control of the shock-chilling procedure. The results in Table X showed a considerable improvement in reproducibility. The ratio of the highest to the lowest yield value was about 1·5 for each of the three oils tested. The third test oil was a centrifuged sample of the second. It had a higher yield value than before treatment. The reason for this is not clear.

TABLE X

Effect of Close Standardization of Shock-chilling Procedure
Condition—Shock-chilling liquid-water (unstirred)
Shock-chilling temperature −50° F

Oil characteristics		Reheat temperature, °F	Yield value (dynes/cm²) at 32° determined at laboratory					
Kinematic viscosity at 100° F cS	IP (upper) pour point, °F		1	2	3	4	5	8
40·6	45	80	120	180	130	170	220	130
		90	190	170	200	290	170	140
		105	110	170	140	200	170	190
		120	150	80	110	190	—	160
43·3	25	80	470	640	290	630	660	470
		90	380	640	580	730	670	510
		105	410	550	520	460	390	530
		120	140	230	—	130	—	210
43·3 *	25 *	80	800	950	—	920	840	—
		90	730	980	—	1110	950	—
		105	660	750	—	570	590	—
		120	—	—	—	170	190	—

* Sample of second oil after centrifuging at 15,000 g.

LIMITATIONS OF THE YIELD VALUE TEST METHOD

The laboratory work on yield value had enabled a test procedure to be developed to a stage where it had a reproducibility that was suitable for specification purposes. However, in the interim, full-scale tests had provided further experience of Admiralty requirements. These trials showed that only very occasionally were tanks containing gelled oil encountered.

In general, depots were found to have developed their own techniques of handling oils which might gel: the normal procedure was to arrange to drain lines. During large-scale tests, which covered a period of four years, only one series of tests was made on a line containing gelled oil, and in this case the conditions were arranged so that a cross line, which would normally be drained, gelled during the winter.

Unheated winter tank temperatures, at which fuel might have to be handled, are compared in Table XI with the flow points and pour points of some Admiralty grade fuel oils. This comparison shows that only in one isolated instance was the handling temperature significantly below the flow point. Thus the full-scale trials did not substantiate the original hypothesis that the fuel oils would have to be handled at temperatures well below their pour points.

TABLE XI

Winter Handling Temperatures of Admiralty Fuel Oil (U.K. Conditions) Compared with Fuel Oil Flow Point

Oil characteristics			Handling temperature in winter trials, °F
Kinematic viscosity at 100° F, cS	IP (upper) pour point, °F	Method VII flow point, °F	
87·7	−20	0	37
109·9	25	10	45
79·0	65	60	44
43·3	25	50	49
40·6	45	40	44

Comparison of the yield values of the oils with the observed handling characteristics in installations showed that an approximate correlation existed between measured yield value and handling properties. It was, however, clear that the handling of fuel oils in surface installations could be much better predicted by viscosity tests under appropriate conditions. A survey of installations showed that the appropriate test temperature was 48° F and not the 32° F envisaged for the yield value test.

Therefore, since it was of prime importance to control the flow properties of fuel oils in shore installations, further development work on the yield value test was suspended. The experience gained in the development of a reproducible yield value test was used to help in developing a suitable viscosity test. However, it was recognized that circumstances might arise in which the handling of fuel oils at sub-pour point temperatures might be called for. The modified

Method XIII test was available to cater for such requirements.

ACKNOWLEDGMENTS

The author thanks the Board of Admiralty and the Chairman and directors of The British Petroleum Company Ltd. for permission to publish this paper. The extensive work of the members of Panel F of the Admiralty Fuels and Lubricants Committee on the development of the test is gratefully acknowledged.

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THE FALLING SPHERE PUMPABILITY TEST FOR BOILER FUEL *

Prepared by J. F. T. BLOTT † (Fellow) and R. G. MARTIN † and presented by J. F. T. BLOTT

SUMMARY

A method of determining the temperature at which a residual oil will have a specified viscosity is described which is simple, comparatively quick, and needs only easily obtained apparatus. Various factors affecting the test are discussed, with the conclusion that no elaborate precautions need be taken in adjusting the apparatus.

INTRODUCTION

Panel F of the Admiralty Fuels and Lubricants Advisory Committee has been concerned with the development of methods which will enable the pumpability of furnace fuel oil to be predicted. It has been shown that a certain heat treatment can be used to bring an oil sample into a condition in which it gives approximately the same viscosity as that of the same oil stored for some years in Admiralty unheated surface storage tanks. The viscosity of the heat-treated oil can then be measured by a viscometer applying a constant rate of shear or a constant shear stress, using a value appropriate to conditions occurring in full-scale operation, but this viscosity measurement requires more skill and experience than can normally be expected in the control laboratories, which will ultimately be carrying out the tests. Hence there is a need for a simplified method of measuring the viscosity.

It is envisaged that, in an Admiralty specification for residual fuel oils, a useful alternative to a figure for the maximum viscosity at a certain temperature would be a maximum temperature for a certain viscosity. This would inform an operator how low the oil temperature could be allowed to fall before difficulties would be experienced in pumping. Now in the case of most Admiralty residual fuels, especially those which are known to be unsatisfactory in pumping, the viscosity/temperature curves become very steep at the lower temperatures. A small change of temperature in this low temperature region corresponds to a large change of viscosity, so that a moderate error in measuring the viscosity corresponds to a trivial error in estimating the corresponding temperature. If, therefore, the test sets out to define a maximum temperature for a certain viscosity, there will be no need for great accuracy in the viscosity measurement. Typical figures would be: if the precision of the maximum temperature for pumping is to be $\pm 1°$ F the corresponding precision in viscosity measurement would have to be ± 10 poises in 20 poises. In the case of an oil which has not this very steep viscosity/temperature curve there would be less precision in the temperature obtained from such a rough viscosity measurement; but this type of oil, having little wax, would not give rise to pumping difficulties anyway, and therefore errors in the specified temperature would be unimportant, so there is no need for great accuracy in viscosity measurements in this case either.

OUTLINE OF METHOD OF VISCOSITY MEASUREMENT

Before the viscosity measurement itself is carried out, the oil is subjected to a test treatment according to the AFLAC method, which is described in the Appendix. The oil is brought to a certain temperature (called the "reheat temperature"), after which it is transferred to a test tube and cooled at a standard rate. During the course of cooling, steel balls are dropped into the oil at regular intervals and the time taken for each descent is measured. This time is related to the viscosity of the oil at the time of measurement. Thus, a viscosity/temperature curve is obtained from which, by interpolation, the temperature for any particular viscosity can be found.

THEORY OF THE METHOD

Stokes' law states that the resistance to movement of a rigid sphere in an unbounded viscous fluid is given

* MS received 29 October 1959.

† "Shell" Research Ltd.

by $6\pi nrv$, where n is the viscosity of the fluid, r is the radius of the sphere, and v is its velocity. A steel sphere falling through such a fluid would therefore acquire a velocity v given by:

$$6\pi nrv = \frac{4}{3}\pi r^3(D - d)g$$

or

$$n = \frac{2\ r^2g(D - d)}{9 \qquad v} \quad . \ . \ . \quad (1)$$

where D is the density of the steel, d is the density of the fluid, and g is the acceleration due to gravity.

This theory has to be modified in the case of a sphere falling in a fluid contained in a relatively narrow, rigid tube. A satisfactory modification to the theory was worked out by Faxen, who obtained equations rather difficult to apply. However, Bacon has presented them in graphical form (*J. Frank. Inst.*, 1936, **221**, 251) which can easily be applied to the problem in hand. Thus the viscosity is given by:

$$n = \frac{2\ r^2g(D - d)\ F}{9 \qquad v} \quad . \ . \ . \quad (2)$$

The correction factor, F, is read from a graph of F against $\frac{r}{R}$, where R is the internal radius of the tube.

The correction factors involved in the present measurements are given in Table I. Since n is inversely proportional to v for a given tube, sphere, and oil density, it can be simply obtained from the time of fall by multiplying the latter by the factor: $\frac{2\ r^2g(D - d)F}{9 \qquad l}$, where l is the length of oil column. It is convenient that this factor should be a small integer, and this can be arranged by choosing a suitable value of l. Thus, in Table I lengths of oil column are quoted which give factors of 1, 2, and 3 respectively.

TABLE I

Constants involved in the Falling Sphere Apparatus

Diameter of sphere, inches	Internal diameter of glass tube, cm	Length of glass tube, inches	F	Length of oil column, cm	Viscosity in poises Time of fall in sec
$\frac{1}{16}$	1·13	4	0·711	6·74	1
$\frac{1}{4}$	1·14	5	0·456	8·65	2
$\frac{1}{8}$	1·18	6	0·149	8·1	3

PRACTICAL DETAILS

In order to determine the time taken for the steel ball to fall through a layer of opaque oil of known thickness, the oil is floated on a layer of water (or, if temperatures lower than 32° F are used, water plus ethylene glycol). The ball can then be clearly seen emerging from the oil layer into the water, and the descent time can be measured within a fraction of a second.

Since the oil in the tube is warmer, during cooling, than the liquid in the cooling bath, the temperature of the oil is measured by means of a thermometer immersed in an identical tube of oil, which, of course, will also be slightly warmer than the bath liquid.

The steel balls are contained in a vessel maintained at the temperature of the cooling bath so that when a viscosity determination is carried out the ball used will be approximately at the temperature of the oil.

THE EFFECT OF SLIPPAGE

Faxen's theory assumed that there was no slippage between the oil and the sphere or between the oil and the tube. This is not the case if the sides of the tube have been wetted by the water before oil has been poured in, and it has been found that the resulting error may be considerable in the case of $\frac{1}{8}$-inch spheres. (It will be even more so in the case of $\frac{1}{4}$-inch spheres.)

Three 4-inch long, $\frac{1}{2}$-inch diameter tubes, designated *a*, *b*, and *c*, were taken. Oil was poured into tube *a* and subsequently water (containing some ethylene glycol) was injected by means of a syringe into the bottom of the tube to a depth of about 2 cm. The same quantity of water was placed in tube *b* and spread around before the oil was added. Tube *c* contained oil with no water at all. Tube *c* was used as a reference tube, tube *a* was used to find what effect on the apparent viscosity, if any, a water layer at the bottom of the tube would have, and tube *b* was used to find the effect of slip. Two series of tests were carried out; one with a light distillate oil *A* and $\frac{1}{16}$-inch spheres, another with a heavier distillate oil *B* and $\frac{1}{8}$-inch spheres. In each case the tubes were immersed in a water bath at room temperature. The repeatability was about one second. In tubes *a* and *b* the time taken for the ball to pass right through the oil was measured. In tube *c* the time taken for the ball to fall to a certain scribed mark was measured. The distance between the air level and this mark was the same as the distance between the air level and the water level in the other tubes. In Table II the results of several tests are averaged.

TABLE II

Effect of Slippage

Oil	Size of sphere	Time of descent (sec)		
		(*a*) Water layer: walls dry	(*b*) Water layer: walls wet	(*c*) Oil alone: no water
A	$\frac{1}{16}$-inch dia	16·2	15·3	15·9
B	$\frac{1}{8}$-inch dia	12·5	9·6	12·2

The effect of the water layer at the bottom of the tube appears to increase the time of descent slightly. The lubrication of the walls by a surface film of water

has a much larger effect, and in the case of $\frac{1}{8}$-inch spheres makes the apparent viscosity too low by about 25 per cent. It is considered necessary therefore to inject the water through the oil to the bottom of the tube by means of a syringe.

THE EFFECT OF SPHERE TEMPERATURE

In an experiment to assess the error arising from temperature differences between the sphere and the oil, several spheres were contained in a tin floating on water heated to about 160° F. The descent-times of spheres in a distillate oil were measured in the usual way, using spheres which were either at the correct temperature or too hot. Table III shows the effect of sphere temperature. The viscosities reported are in each case the mean of several measurements. The repeatability was about one second.

TABLE III

Effect of Sphere Temperature

Temperature of oil, °F	Descent time, sec			
	$\frac{1}{8}$-inch spheres		$\frac{1}{16}$-inch spheres	
	Spheres at 62° F	Spheres at 160° F	Spheres at 62° F	Spheres at 160° F
61·5	7·1			
61·6		4·8		
61·7	6·8			
61·8			21·0	
62·0				19·2
62·0			20·8	

These results show that a temperature discrepancy of 100° F causes viscosity errors of about 8 per cent in the case of the $\frac{1}{16}$-inch spheres and about 35 per cent in the case of the $\frac{1}{8}$-inch spheres. It is considered advisable therefore to bring the $\frac{1}{8}$-inch spheres to the correct temperature before they are used in viscosity measurement.

THE EFFECT OF TILT OF TUBES

A tube containing distillate oil was first held vertical and then inclined by about $2\frac{1}{2}$°. This inclination was visually very obvious. Table IV summarizes the times of descent of $\frac{1}{16}$-inch spheres between scribed marks in a $\frac{1}{2}$-inch dia tube. It is evident that (in the case of a Newtonian oil at least) the results are not critically dependent upon inclination.

TABLE IV

The Effect of Tilt

Temperature, °F	Descent time, sec	
	Tube vertical	Tube tilted
64·2	8·63	
64·2		8·58
45·2	21·8	
45·2		21·9

THE EFFECT OF NON-CENTRALITY OF SPHERE

To investigate the importance of positioning the sphere in the tube so as to fall centrally, experiments were carried out on five residual fuel oils which had been subjected to a heat treatment before test. One tube of oil was fitted with a funnel-shaped dispenser which ensured a central positioning of the sphere, while another tube, filled with identical oil, was fitted with a similar dispenser which was displaced halfway between the centre and the outside of the tube. At stabilized temperatures, viscosity measurements with $\frac{1}{8}$-inch spheres were carried out on oil in each tube until successive viscosity values ceased to drop. In Table V the viscosities as measured in each tube are given. It is seen that the difference between the results is small, and it is concluded that it is of little importance to drop the sphere exactly centrally.

TABLE V

Equilibrium Viscosities in Tubes with Central and Displaced Dispenser

Oil	Temperature, °F	Equilibrium viscosities, poises	
		Central dispenser	Displaced dispenser
1	47·2	16·2	13·9
2	48·3	16·2	17·4
3	51·7	13·1	12·8
5	37·0	10·3	10·0

CHOICE OF THERMOMETER

During cooling in a tube, the oil near the outside of the tube is cooler than that in the centre. But as the ball falls down the tube, oil is forced to flow not only in the immediate vicinity of the sphere but also (less rapidly) everywhere in the cross-section. The apparent viscosity of the oil as measured by a falling sphere will therefore be higher than the viscosity of the oil in the centre of the tube, and will correspond, not to the temperature at the centre of the tube, but to some lower temperature, which must be measured in the test. If the bulb of the thermometer has too small a diameter the indicated temperature will be too high, whereas if it has too large a diameter the indicated temperature will be too low. The best type of thermometer was chosen by experiment.

Four 4-inch long, $\frac{1}{2}$-inch dia tubes were used. The first three tubes were filled with a distillate oil and thermometers were inserted, positioned by corks. The thermometers were of different types. One was an IP 15F and had a bulb diameter of $\frac{1}{4}$-inch; the

bulb diameters of the others were $\frac{1}{16}$ inch and $\frac{1}{32}$ inch. The fourth tube was filled with the same oil but was without a thermometer. Marks were scribed on it

TABLE VI

Determination of the Optimum Thermometer Bulb Diameter

(a) *Measurements During Cooling*

Thermometer readings				
$\frac{1}{16}$-inch dia bulb, ° F	$\frac{1}{4}$-inch dia bulb (IP 15F), ° F	$\frac{1}{32}$-inch dia bulb, ° F	Water bath, ° F	$\frac{1}{16}$-inch sphere descent time, sec
—	—	—	97·5	1·8
98·8	97·5	98·6	95	2·4
—	—	—	92·5	2·65
93·8	92·3	92·8	90	3·0
—	—	—	87·5	3·1
88·5	87·5	88·3	85	3·4
—	—	—	82·5	3·7
83·5	82·2	83·3	80	4·15
—	—	—	77·5	4·6
78·0	77·0	77·4	75	5·05
—	—	—	72·5	5·75
72·0	71·2	72·0	70	6·4
—	—	—	67·5	7·1
67·5	66·5	67·1	65	7·85
—	—	—	62·5	9·0
61·8	61·2	61·7	60	10·0
—	—	—	57·5	11·3
56·8	56·1	57·2	55	12·8
—	—	—	52·5	14·4
51·8	51·2	51·8	50	16·2
—	—	—	47·5	18·45
46·8	46·0	46·0	45	21·3

TABLE VII

Determination of the Optimum Thermometer Bulb Diameter

(b) *Measurements at Steady Temperatures*

Thermometer readings						
$\frac{1}{16}$-inch dia bulb, ° F	$\frac{1}{4}$-inch dia bulb (IP 15F), ° F	$\frac{1}{32}$-inch dia bulb, ° F	Water bath, ° F	$\frac{1}{16}$-inch sphere descent time, sec		
45·0	45·0	45·1	45·0	22·0	22·0	21·8
50·0	49·9	50·0	50·0	17·0	17·0	17·0
55·0	54·9	55·2	55·0	13·3	13·4	13·2
65·0	64·7	64·5	64·95	8·4	8·4	8·3
75·0	74·7	74·7	75·0	5·4	5·4	5·5

6·78 cm apart. The tubes were immersed in the usual way in a water bath. The water bath was heated to 100° F and then cooled by the standard method (see Appendix). After every 2·5° F drop in water-bath temperature the viscosity of the oil was measured with a $\frac{1}{16}$-inch sphere, and simultaneously with alternate measurements of viscosity the three thermometers immersed in oil were read. After the bath had cooled to 45° F the bath was reheated, and at various steady temperatures the viscosity and temperature measurements were repeated. The results are shown in Tables VI and VII and Fig 2, and show that the

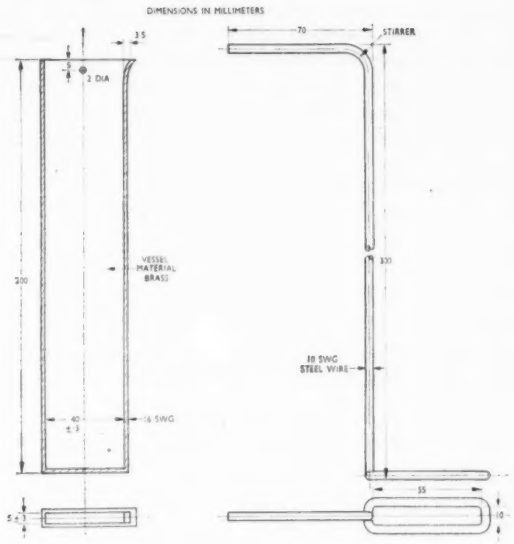

FIG 1

SPECIAL BRASS VESSEL FOR HEAT TREATMENT OF OIL SAMPLE

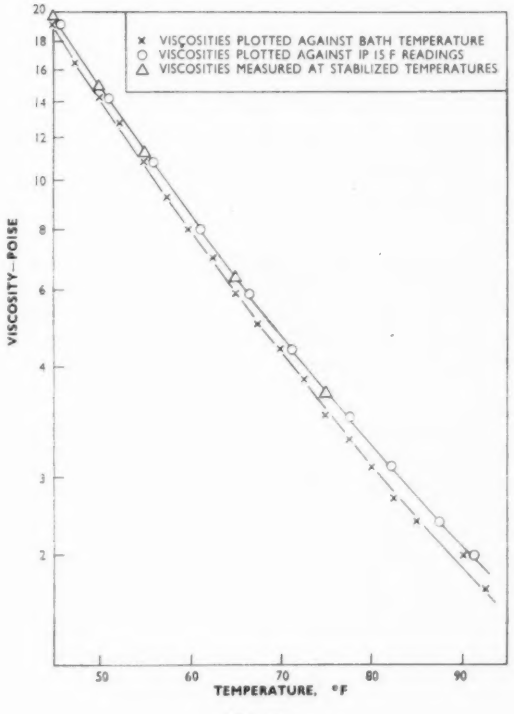
× VISCOSITIES PLOTTED AGAINST BATH TEMPERATURE
○ VISCOSITIES PLOTTED AGAINST IP 15 F READINGS
△ VISCOSITIES MEASURED AT STABILIZED TEMPERATURES
VISCOSITY—POISE
TEMPERATURE, °F

FIG 2

FALLING SPHERE VISCOSITY MEASUREMENTS ON A DISTILLATE OIL

temperature corresponding to the apparent viscosity is very nearly that indicated by the IP 15F thermometer. The temperature indicated by a narrow ($\frac{1}{16}$-inch dia) bulb thermometer is, as expected, high. The temperature of the $\frac{3}{32}$-inch dia bulb thermometer is also high, contrary to expectations; the reason for this is not known. The thermometer recommended for the test is an IP 15F.

THE FINALIZED TEST

The factors influencing the result, described above, were taken into account in writing a final version of the test. This test, together with the details of the heat treatment, is given in the Appendix.

REPEATABILITY AND REPRODUCIBILITY

To assess the repeatability of the method, tests using $\frac{1}{16}$-inch balls were made with five Admiralty oils. The falling sphere measurements were made simultaneously on two samples of the same oil. The results obtained are given in Table VIII.

TABLE VIII

Repeatability of $\frac{1}{16}$-inch Falling Sphere Measurements

Oil	Temperature for 20 poises, ° F	
	Sample 1	Sample 2
36	55·0	55·5
37	50·0	52·5
12	64·0	64·0
22	51·5	52
30	47·5	47·5

The evidence from these experiments is that the repeatability is better than $\pm 1{\cdot}3°$ F. A separate series of experiments was carried out with $\frac{1}{8}$-inch steel balls; the results obtained are shown in Table IX.

TABLE IX

Repeatability of $\frac{1}{8}$-inch Falling Sphere Measurements

Oil	Temperature for 20 poises, ° F	
	Sample 1	Sample 2
36	48	48
37	49	48
12	54·5	53
30	37	36

The repeatability as assessed by these measurements is $\pm 0{\cdot}75°$ F or better. In tests with both $\frac{1}{16}$-inch and $\frac{1}{8}$-inch spheres, therefore, the precision of the viscosity measurement appears to be satisfactory. Errors may, however, be introduced through lack of repeatability of the heat treatment, but that is not the subject of the present paper.

To find the reproducibility of the method, five laboratories took part in a co-operative programme in which four oils were tested by the falling sphere method outlined above. The maximum temperature for a viscosity of 25 poises was reported, using both $\frac{1}{16}$-inch and $\frac{1}{8}$-inch spheres. The results are shown in Tables X and XI.

TABLE X

Co-operative Test Results on Four Oils Using the $\frac{1}{16}$-inch Falling Sphere Test

Oil	Maximum temperature for 25 poises, ° F			
	Lab A	Lab B	Lab C	Lab D
36	48·0	47·0	50·5	—
37	50·0	46·5	51·0	49·0
12	56·0	55·5	56·5	57·0
22	44·0	42·5	44·5	43·0

TABLE XI

Co-operative Test Results on Four Oils Using the $\frac{1}{8}$-inch Falling Sphere Test

Oil	Maximum temperature for 25 poises, ° F			
	Lab A	Lab C	Lab D	Lab E
36	42·5	43·5	50 *	45·0
37	44·3	46·0	40·0	45·0
12	52·0	49·0	50·0	52·0
22	41·0	41·5	40·0	40·0

* Probably an incorrect sample.

In the worst case there is a discrepancy of 6° F between the lowest and the highest temperature found. This can be regarded as indicating very good reproducibility for the viscosity measurements, since part of the discrepancies must be due to the heat treatment and not to the viscosity test.

BREAKDOWN OF VISCOSITY

When an oil of the class being considered is heat treated and then steadily cooled, without being sheared, a wax structure builds up in it progressively, and the viscosity of such an oil is greater than that of the same oil sheared during cooling.

In Table XII viscosity measurements are given on an oil sample which was tested periodically during cooling, and also on another sample of the same oil unsheared until the test temperature was reached. The latter sample (called " undisturbed sample ") was brought to the final temperature and a number of spheres dropped through it at that temperature until successive descent times were equal. The number of drops necessary to achieve this is given in Table XII,

as also is the final viscosity achieved. The viscosity estimated for the same final temperature on the sample which was periodically tested during cooling is also recorded.

It will be seen that, except in the case of oil No 12, there is an appreciable breakdown of the undisturbed sample on testing and that the equilibrium value is in good agreement with that measured at the same temperature on the sample tested at regular intervals during cooling.

The method therefore gives test results which have an empirical correlation with viscosity measurements in which shearing to equilibrium is carried out only at the test temperature.

Table XIII shows the progressive breakdown in falling sphere tests on a sample of oil No 37 cooled

TABLE XII

Comparison between Results Obtained by the $\frac{1}{16}$-inch Falling Sphere Method on Undisturbed and Disturbed Samples

	Oil 36	Oil 37	Oil 12	Oil 22	Oil 30
Temperature, ° F .	53·3	51·0	59·3	50·6	47·1
Undisturbed sample					
Initial viscosity, poises .	44·0, 44·8	40·0	27·5	41·6, 46·2	31·0, 31·2
Number of passes .	14 14	8	3	14 17	8 8
Final viscosity, poises .	30·0, 34·8	28·2	28·6	33·3, 38·4	20·0, 19·3
Disturbed sample					
Viscosity, poises .	30·4, 30·4	19·5, 42·8	28·5, 27·0	28·8, 31·5	21·4, 19·0

TABLE XIII

Progressive Breakdown by Shearing with Falling Sphere

Temperature = 51·0° F

Number of spheres dropped	Viscosity, poise
1	40·0
2	32·6
3	30·6
4	29·1
5	29·0
6	27·8
7	29·2
8	28·2

without disturbance to 51° F. It appears that most of the breakdown occurs during the first two or three passages of the sphere.

EFFECTIVE SHEAR STRESS

According to the simple Stokes theory, the maximum shear stress exerted on the oil by the passage of the sphere is at the equator of the sphere and is given by:

$$\text{shear stress} = \tfrac{1}{8} r \,.\, g \,.\, (D - d)$$

using the symbols defined above. This formula gives as shear stress in the case of the $\frac{1}{16}$-, $\frac{1}{8}$-, and $\frac{1}{4}$-inch spheres of 179, 358, and 715 dynes/cm², respectively. This theory, however, has to be modified to allow for the constraint due to the walls of the tube. In addition, it is valid only for Newtonian liquids, and will lead to erroneous conclusions if applied to shear-stress-sensitive residual fuel oils. The viscosities of these oils when sheared throughout their volume, *e.g.* in a coaxial viscometer, may be much lower than those indicated by the falling sphere test, which exerts a very small shear stress on the bulk of the oil and therefore fails to break down the bulk of the structure. It is necessary to carry out experiments to assess the effective shear stress in the falling sphere test. The effective shear stress is defined as that shear stress which, when applied to the oil in a coaxial viscometer, gives an equilibrium value of viscosity equal to that obtained by the falling sphere test at the same temperature.

The oil was heat-treated in the usual way and placed in a constant shear stress coni-cylindrical viscometer. The viscometer was cooled at 1° F/min to a temperature which had been determined by a previous falling sphere test—the temperature at which the viscosity was 25 poises by the latter test. The temperature was held constant for an hour, then a small shear stress was applied. When sufficient time had elapsed for the speed of the rotor to become constant the viscosity was noted and the shear stress was increased. When the speed had again become constant the viscosity was again noted and the speed increased, and so on. From these measurements a graph of viscosity v shear stress could be plotted, and by interpolation the shear stress giving 25 poises could be found. This was the effective shear stress in the falling sphere test.

Using this method, the effective shear stresses with three heat-treated oils and two oils without heat treatment were determined, and are shown in Table XIV.

TABLE XIV

Effective Shear Stresses on Falling Sphere Test

Oil	Temperature of test, ° F	Effective shear stress, dynes/cm²	Size of sphere, inches
37 (treated)	44·3	135	$\frac{1}{4}$
12 (treated)	41·0	270	$\frac{1}{4}$
22 (treated)	52·0	165	$\frac{1}{4}$
37 (untreated)	42·0	38	$\frac{1}{8}$
30 (untreated)	49·3	20	$\frac{1}{16}$

From this evidence it seems that the effective shear stress is very much lower than the maximum stress calculated above, and is least in the case of oils known to be most non-Newtonian. Thus the falling sphere test is biased in favour of non-waxy oils. This may be an advantage in some applications; the test may

be regarded as providing a safety factor which discriminates against oils likely to give pumpability troubles.

COMPARISON WITH FIELD MEASUREMENTS

Oils have been sampled at low temperatures from storage tanks during the field trials described elsewhere and immediately tested for viscosity in a coaxial cylinder viscometer. The results obtained on four oils are given in Figs 3–6, together with the ¼-inch falling sphere measurements carried out later on the same oils after heat treatment. The falling sphere tests tend to give viscosities rather low compared with those given by the viscometer.

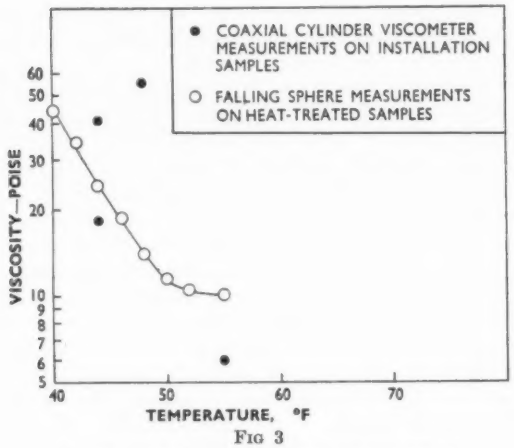
COAXIAL CYLINDER VISCOMETER MEASUREMENTS ON INSTALLATION SAMPLES
FALLING SPHERE MEASUREMENTS ON HEAT-TREATED SAMPLES
VISCOSITY—POISE
TEMPERATURE, °F

Fig 3

¼-INCH FALLING SPHERE TESTS ON OIL NO 36 CONDITIONED BY AFLAC HEAT TREATMENT

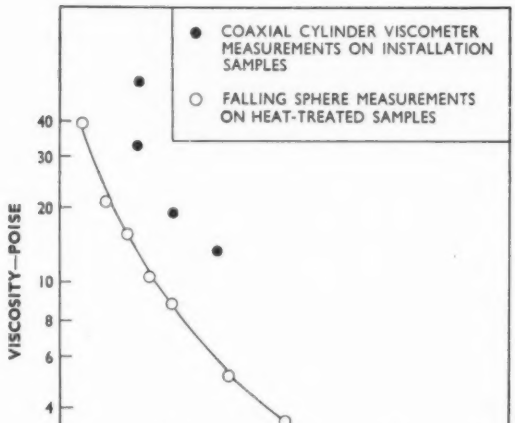
COAXIAL CYLINDER VISCOMETER MEASUREMENTS ON INSTALLATION SAMPLES
FALLING SPHERE MEASUREMENTS ON HEAT-TREATED SAMPLES
VISCOSITY—POISE
TEMPERATURE, °F

Fig 4

¼-INCH FALLING SPHERE TESTS ON OIL NO 37 CONDITIONED BY AFLAC HEAT TREATMENT

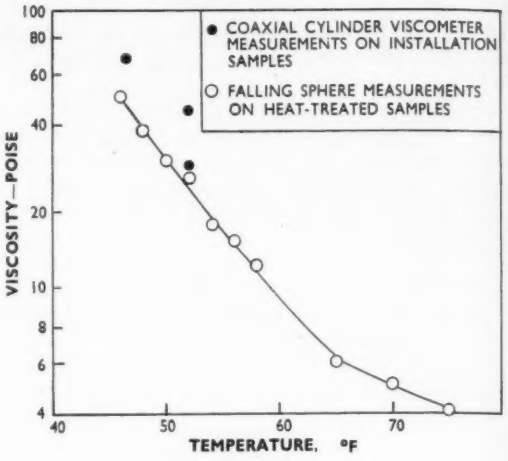
COAXIAL CYLINDER VISCOMETER MEASUREMENTS ON INSTALLATION SAMPLES
FALLING SPHERE MEASUREMENTS ON HEAT-TREATED SAMPLES
VISCOSITY—POISE
TEMPERATURE, °F

Fig 5

¼-INCH FALLING SPHERE TESTS ON OIL NO 12 CONDITIONED BY AFLAC HEAT TREATMENT

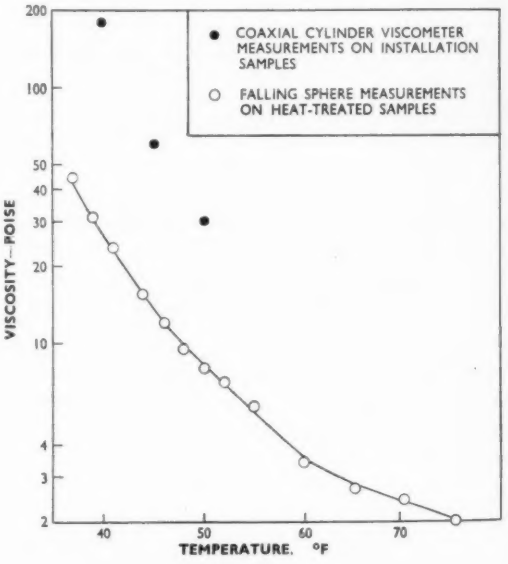
COAXIAL CYLINDER VISCOMETER MEASUREMENTS ON INSTALLATION SAMPLES
FALLING SPHERE MEASUREMENTS ON HEAT-TREATED SAMPLES
VISCOSITY—POISE
TEMPERATURE, °F

Fig 6

¼-INCH FALLING SPHERE TESTS ON OIL NO 22 CONDITIONED BY AFLAC HEAT TREATMENT

CONCLUSIONS

The falling sphere test is a simple, comparatively rapid method, requiring only a small sample of oil and simple apparatus. Great care in setting up the apparatus is unnecessary. The results obtained from it are satisfactorily precise, but tend to discriminate against waxy oils.

APPENDIX

THE FALLING SPHERE PUMPABILITY TEST FOR BOILER FUEL

1. *Introduction*

(*a*) This test is used to determine the Pumpability Temperature of an oil.

(*b*) The pumpability temperature of an oil is the temperature at which the oil, after it has been heat treated in a prescribed way, has a viscosity of 25 poises.

(*c*) The pumpability temperature is intended to indicate the lowest temperature at which an oil in its worst state can be pumped at full output under service conditions.

2. *Outline of Method*

The sample of oil in a special brass vessel is heated to 165° ± 5° F, and shock-chilled to 32° F. It is then heated to and maintained at one of a series of reheat temperatures for 30 minutes, after which the oil is transferred to a test tube and cooled at a standard rate. The viscosity of the oil is then determined by the falling sphere method at intervals during the cooling.

The test is repeated using different reheat temperatures between 60° and 160° F with the object of finding which reheat temperature gives the highest value for the temperature corresponding to a viscosity of 25 poises. The latter temperature is reported as the Pumpability Temperature.

3. *Apparatus*

(a) *Special Brass Vessel*

Special brass vessel as in Fig 1, measuring 0·5 cm × 4 cm × 20 cm (internal dimensions), with a wall thickness of 0·159 cm ($\frac{1}{16}$-inch).

(b) *Thermometers*

IP 15F or ASTM 9F-53 are suitable for all operations.

(c) *Preheating Bath*

Water bath of any suitable size and shape to accommodate the special brass vessel, equipped with means of maintaining its temperature at 165° ± 5° F.

(d) *Chilling Bath*

Bath of any suitable size and shape, to accommodate the special brass vessel, filled with a mixture of approximately 3 volumes of crushed ice to 2 volumes of water. A looped stirrer made of 0·24 cm ($\frac{3}{32}$-inch) wire as shown in Fig 2 should be provided to agitate the ice-water adjacent to the brass vessel.

(e) *Reheat Bath*

Water bath of any suitable size and shape to accommodate the special brass vessel, equipped with means of maintaining its temperature at the required reheat temperature, which lies between 60° and 160° F. This bath should be capable of maintaining the desired temperature with an accuracy of ±2° F.

(f) *Glass Test Tubes*

Glass test tubes 1·18 ± 0·04 cm ($\frac{7}{16}$-inch) internal diameter and about 15 cm (6 inches) long, with a scribed horizontal line at a distance of 8·4 cm from the bottom of the tube.

(g) *Steel Balls*

Steel balls, 0·635 cm ($\frac{1}{4}$-inch) diameter.

(h) *Controlled Rate of Cooling Bath*

Glass vessel of about 17 cm internal diameter and about 19 cm deep supported on three distance pieces, about 4 cm high, in a larger vessel at least 21 cm in internal diameter and 10 cm deep (gas evolved from the solid carbon dioxide used as coolant will escape more readily from beneath the glass vessel if this is tilted slightly by making one of the distance pieces somewhat taller than the others). The inner vessel is filled with water to within about 3 cm of the rim, and the outer vessel is filled to a depth of 6·5 cm with *iso*propyl alcohol. The inner vessel is provided with a vigorous mechanical stirrer.

The controlled rate of cooling is obtained by adding solid carbon dioxide to the outer bath of alcohol to maintain its temperature at about 0° F.

(i) *Syringe and Capillary Tube*

Syringe fitted by means of a detachable ground joint to a metal capillary tube about 23 cm long and with an internal diameter of about 0·08 cm ($\frac{1}{32}$-inch), to deliver about 4·5 ml of liquid.

(j) *Stopwatch*

Stopwatch graduated in $\frac{1}{5}$ second.

(k) *Containers for Steel Balls and for Glycol/Water*

Convenient vessels suspended in the controlled rate of cooling bath for holding at least 25 of the steel balls, and at least 9 ml of the glycol/water mixture (see *Materials*, below), to bring them to the correct temperature.

4. *Materials*

(*a*) 1 : 1 mixture of ethylene glycol and distilled water containing a trace of detergent.

(*b*) Solid carbon dioxide.

5. *Sampling and Handling Sample*

The minimum quantity of oil required for the complete test is about 200 ml. Particular care must be taken to ensure that this is fully representative of the bulk sample. In order to obtain the test sample, warm the bulk sample to at least 120° F, taking care not to heat any part of it to above 165° F. Shake the bulk sample and fill any suitable container.

6. *Procedure*

(*a*) Heat the whole test sample in a water bath maintained at a temperature of 165° ± 5° F until the oil temperature reaches at least 120° F. Shake the sample and fill the special brass vessel to within about 2·5 cm from the top. Immerse the brass vessel to within 2·5 cm of its top in the preheating bath maintained at 165° ± 5° F.

(*b*) After 15 minutes remove the brass vessel from the preheating bath and plunge it *immediately* into the chilling bath. Keep the brass vessel in the chilling bath for exactly 10 minutes, and during the first *5 minutes* of this time agitate the liquid in contact with the walls of the brass vessel at the rate of at least one up-and-down stroke per second with the special looped stirrer.

(*c*) Remove the brass vessel from the chilling bath and immerse it, to within 2·5 cm of its top, in the heat-treatment bath maintained at the reheat temperature of 90° ± 2° F. Keep it in this bath for 30 minutes.

(*d*) Into the controlled rate of cooling bath maintained at the reheat temperature (90° ± 2° F) in this case, and at least 5 minutes before these 30 minutes have elapsed, place two dried test tubes vertically side by side immersed to within 1 cm of their rims. Place 25 steel balls in one of the containers (see *Apparatus*, section 3 (*k*)) and fill the other container with the glycol/water mixture.

(*e*) Pour oil from the brass vessel treated as in (*c*) into both test tubes to bring the oil level to that of the scribed line.

(*f*) With the syringe inject about 4·5 ml of the glycol/water mixture, drawn from the container placed in the controlled rate of cooling bath, at the bottom of each tube. Insert an IP 15F thermometer to a depth of 5 cm into the oil layer in one of the tubes.

(*g*) Add solid carbon dioxide to the alcohol surrounding the controlled rate of cooling bath in such a way as to bring the alcohol's temperature rapidly to, and to keep it at, 0° F, so cooling the water in the inner vessel from the reheat temperature. Keep the alcohol well agitated by judicious addition of solid carbon dioxide.

(*h*) When the temperature indicated by the thermometer immersed in the oil layer in one of the tubes falls to a value of 5° F less than the reheat temperature, *i.e.* to 85° F when the reheat temperature is 90° F, take one of the steel balls

from its container and drop it into the other tube and measure the time in seconds for the ball to fall through the oil layer. Repeat this operation at intervals of 5° F during the cooling until the time of fall exceeds 3 seconds, and then make further measurements at intervals of 2° F until the time of fall exceeds 15 seconds, when the test is discontinued.

(*i*) Plot the times of fall in seconds against the temperature of the oil when the ball was released. Estimate by interpolation the temperature corresponding with a time of fall of 8·3 seconds (this time of fall corresponds with a viscosity of 25 poises).

(*j*) Repeat the whole test using other reheat temperatures selected from the series 60°, 70°, 80°, 90°, 105°, 120°, 140°, 160° F in order to determine the reheat temperature giving the maximum value of the oil temperature corresponding with a time of fall of 8·3 seconds.

Note: By suitable timing it is possible to make simultaneous determinations for different reheat temperatures.

(*k*) Having established the reheat temperature giving the maximum value of the oil temperature corresponding with a time of fall of 8·3 seconds, make a repeat determination using this reheat temperature. The results of the two duplicate tests should agree within ±2° F.

7. *Reporting*

Report the mean of the temperatures for a time of fall of 8·3 seconds in the duplicate tests described in (*k*) above as the Pumpability Temperature.

DISCUSSION

Dr C. M. Cawley: Professor Sellers has told me that the Panel believe that the achievements of their work can be summed up very briefly by three points, and I think you will be as interested as I was to hear these.

The first point concerns viscosity measurement. A fund of knowledge and information has been acquired about existing equipment and the behaviour of furnace fuel oils in that equipment; as a result, it is possible, for specification purposes, to lay down a realistic pumpability requirement in terms of a viscosity determined at a certain temperature under defined conditions of shear.

The second point concerns the prediction of the behaviour of oils in storage. A procedure has been worked out for the heat treatment which will bring certain classes of freshly-prepared fuel oils to the viscosity condition they would have after prolonged storage exposed to surface ambient temperatures. This is the Method XV we have been hearing about. It is not claimed that Method XV is universally applicable to all oils of whatever origin, but I think it is fair to say that it does apply to a large majority of the oils in which the Admiralty are directly interested. The Panel is extending the work to determine the general applicability of the procedure to other oils.

The third point is the substantial contribution the work has made to the fundamental knowledge of the rheological properties of thixotropic substances.

W. J. van Kerkvoort (Koninklijke/Shell-Laboratorium, Amsterdam): I would like to ask whether there is anything known about the repeatability of the viscosity measurements, including the thermal pretreatment.

Dr D. Wyllie (Admiralty Oil Laboratory): We have done some early work on this. Although I will not say that we have established it yet, at the viscosity level we were dealing with, which was about 18 poise, we got a reproducibility of something like 3 poise, probably equivalent to less than one degree Fahrenheit.

N. S. Rae (Esso Research Ltd): I was very interested indeed in Mr Ackroyd's paper, and in particular in the part dealing with the chemistry of the system as opposed to its rheology. In his remarks at the first session, Dr Monkhouse indicated that he felt that there were quite a number of leads which might well be followed up on the chemical side, and I think Mr Ackroyd's work adds point to this comment. The effect of asphaltenes on the strength of the structures developed seems to me to be extremely important, and it does seem a pity that the work should have been allowed to lapse, rather than followed up very vigorously, because the whole clue to the behaviour of these systems may lie in the chemistry of the asphaltenes, resins, and wax present in the product.

The X-ray work reported showed that a sample of oil treated at two different pre-heat temperatures contains the same amount of crystalline wax, although the optical microscope was not able to detect the wax crystals in one case. Now, here again is a lot of food for thought. I do not think Mr Ackroyd actually said whether he had done similar work on samples taken from the field—but it seems to me that it would be a very logical thing to want to do. What sort of crystals are present in these oils from the field? What sort of crystal sizes are experienced in field samples when they are at their maximum or minimum fluidity? Here again, one might get a very useful clue from the chemistry of the system, leading towards the determination of the proper method of treating these samples, in order to bring them into a similar condition to that achieved in practice.

In conclusion, I think Mr Ackroyd's work gives some useful leads which would be very worthwhile following up.

G. C. Ackroyd (DSIR, Fuel Research Station): I am sorry that the work was not completed. We at the Fuel Research Station have got a mass of information, much more than we have presented here. You at Esso are also responsible for some of this; I think, I may be wrong here, but am I at liberty to talk about the inoculation experiments. What we were hoping for at the Fuel Research Station was to get one unified theory for all the odd facts that we now have, and which we have not published, because it did not finally lead to what we hoped it would.

As an instance, take the inoculation theory. One method of getting either a high pour point condition or a low pour point condition is by re-heating to 105° or 140° F respectively. Another way of getting the high pour point condition, and if anybody can explain what causes it one more piece of the jig-saw can be fitted, is to heat an oil up to 170° or any other temperature above 140°. When the temperature has fallen to 100° to 110° F, inoculate it with a trace of oil in the high pour point condition, and the whole lot ends up in the high pour point condition. Whereas, had the oil been allowed to fall from 170° without this inoculation it would have ended up in the low pour point condition. And we think that a certain amount of our earlier work was invalidated because thermometers are as often as not just wiped with a cloth, and we have probably, without knowing it, been inoculating these oils and getting false pour points. And I imagine a lot of other people have been doing that too.

That is one of the points that has to be tied up,

and I am as disappointed as anybody that the chemistry of this subject has not been fully worked out. However, the difficulties of examining oils in the "as received" condition are great. We carried out examinations of such oils under the microscope, and perhaps it is fair to say that, in general, the wax aggregates in oils in the high pour point state, which have been naturally aged, are very large aggregates, but there are very few of them. They give the impression that they have very little to do with the rheological properties of the oil. You cannot easily take X-ray diffraction pictures of these oils because: (*a*) the X-ray equipment cannot be taken to the depot, and (*b*) even if it was, by the time the oil had been placed in the X-ray diffraction camera and bombarded with X-rays, I am sure it would not be in the same stage as when the investigation was started.

Dr C. M. Cawley: There is one question I would like to ask. As I understand it, the treated oil with the large wax clusters in it is the oil in a low pour point condition, *i.e.* it is readily pumpable. The mention you make of examining in the same way an oil in a natural condition is when it has been stored for long periods, and in which very large aggregates of wax are often present. So here we have an oil which is not readily pumpable and which contains large wax clusters. These two facts seem to be in conflict. Can you explain that?

A. G. Lowe (DSIR, Fuel Research Station): In addition to the large aggregates, there is a considerable number of small crystals. I think that in the alternate warming up and cooling down of the oil, some of the wax is dissolved and then, later, comes out of solution again. Some of this precipitated wax helps to form the large aggregates and the rest remains as the small crystals.

Dr C. M. Cawley: It does at least underline what Mr Rae was saying. It would be very interesting to make further studies of stored oils in their natural condition, since the one you have examined was found to contain these large aggregates of wax crystals.

G. C. Ackroyd: The point I did not stress in my own paper was that the structure we build up in oils by pretreating them so as to obtain them in the high pour point condition probably bears no resemblance at all to the type of structure built up during natural storage. We cannot stress that too much. Our method is only a method of simulating the rheological condition, but it does not, I am sure, simulate the exact colloidal structure of the naturally aged oil.

Professor F. Morton (Manchester College of Technology): I was a little puzzled by Fig 5 in Mr Ackroyd's paper, and the sentence which says "in relation to the oil which is asphaltene and resin free, which produces very anomalous results when tested in a coaxial cylinder viscometer." The results for this particular oil are only anomalous by comparison with the other oils in Fig 5, but the actual behaviour of the asphaltene-resin free sample is that to be expected of a thixotropic substance. Once the initial yield value of the gel has been exceeded, the oil will flow with increasing velocity for a given applied pressure. This behaviour is commonly met with in drilling muds, for example.

G. C. Ackroyd: I must say that I had assumed that was due to the type of flow, and had more of less dismissed it as a completely anomalous result.

C. V. Hill: I have in my mind that some time ago, between 1922 and 1927, we did an experiment at Llandarcy on the full scale. But we took the Persian crude which we then had, which of course would be Masjid-i-Sulaiman with about 10 per cent wax, and only 1 per cent of asphalt. It was distilled in the way we did in those days to about an 80 per cent residue. Then we poured it through activated bauxite, and that absorbed the asphalt, and I think the resins.

What we got out was a nice clean yellow liquid which as soon as it cooled to atmospheric temperature went solid. When warmed up the wax dissolved bit by bit, the change in viscosity was enormous, and once the wax was all fully dissolved, it was an exceedingly mobile liquid. So if you change your temperature by, say, one degree Fahrenheit, you may get an enormous difference in viscosity on this kind of fuel. Once you take the wax and resin out of that kind of oil, you have got something which changes its viscosity very rapidly with temperature.

T. C. Davenport: I would like to emphasize the point made by Mr Ackroyd that the colloidal state of an oil after laboratory pre-treatment procedures is not the same as that after long-term storage in unheated tanks. Mention might be made here of electrical conductivity measurements made on fuel oils at the Fuel Research Station (*J. Inst. Petrol.*, 1955, **41**, 229–34). This work indicated that in laboratory pre-treated oil the main structure was due to an interlocking network of wax crystals, whereas in stored oils the structure was due to the presence of asphaltene-resin micelles in some form of association with the wax.

I would also like to describe work we have carried out at the Sunbury Research Centre which confirms the X-ray work. To find out whether there was any change in the solubility of the wax with change in fluidity, very accurate density measurements were made on fuel oils in the maximum and minimum fluidity conditions. Since the density of precipitated and dissolved wax is not the same, any change in solubility would be shown by a change in density. However, in all the work the density at a given temperature was independent of the fluidity state of the oil, showing that it is a change in wax crystal structure rather than a change in solubility which effects the flow properties.

In the model suggested to explain the behaviour of thixotropic fuel oils, described in the paper by Sellers and Wyllie, there are two points which I feel are contrary to experience. First, the theory indicates that at any time t the oil has a yield stress $P_y(t)$. In practice, once an oil has yielded and flow has commenced there is no measurable yield value. Secondly, the theory indicates that after infinite time the viscosity of the fuel oil will reach an equilibrium value μR independent of the applied shear stress. In practice, there always appears to be a marked dependence of viscosity on applied shearing stress no matter how long the oil has been sheared.

J. W. Clarke (Esso Petroleum Co. Ltd): I recall from the early days of the IP Fuel Oil Flow Panel that you, Mr Chairman, and Mr Ackroyd placed considerable importance on trying to get an oil into its original birth form, *i.e.* to take oil which had been in the field for some time and reconstitute it by a heat treatment cycle to bring it back to its original birth form at the refinery. Although some work on these lines was carried out by the Fuel Research Station, I believe it lapsed. In view of the importance which was attached to such work, I wonder if you could tell us why that particular avenue was not further explored.

G. C. Ackroyd: What we did do, in conjunction with the Shell Petroleum Co., was to go to one of their refineries and obtain samples of everything that went into a fuel oil. In addition, we were given full details of the blending procedure employed at the refinery. We took these components back to the laboratory and attempted to blend oils to the Shell formula; the resultant blend did fairly closely resemble the refinery blend in its aging properties. We also varied the procedure to the extent of allowing the various components to be mixed in the same proportions but in different orders and at different temperatures. If I remember correctly, the final temperature of the mixed residue and re-cycle oil was of the utmost importance. If this temperature was below a certain figure, a blend with a high initial pour point was obtained; if above this particular temperature, a blend with a low pour point was obtained.

Thus the blending appears to determine how an oil is going to behave on subsequent storage. It seems that a low pour point condition can be partly stabilized by suitable choice of blending conditions.

J. F. T. Blott (Shell Refining Co. Ltd): As chairman of the IP Flow Panel I would like to say that what Mr Ackroyd has been referring to has been incorporated in a report of the work of the Panel, which at long last has come to fruition, and in the very near future will be circulated to the members of the committee. It may be that the committee will decide that this should be published.

J. F. Hutton ("Shell" Research Ltd): I have some comments to make on Professor Sellers' paper. I agree with remarks made earlier in the discussion about the value p_y, *i.e.* the variable yield stress, and its decrease to zero at infinite time. I think there is evidence that breakdown reaches an equilibrium with the re-formation of structure, rather than continuing to a complete degradation in infinite time. I wonder what evidence Professor Sellers has for the assumption in the preamble to his theoretical section that p_y tends to zero.

A second point concerns the application of the modified Bingham equation, equation (13). It seems that for the calculation of μ_i from experimental results the applied stress p is divided by the rate of shear S. But according to equation (12) this is a valid procedure only if p_e is zero. Is this a correct interpretation of what has been done? If so, why has p_e been put equal to zero?

The third point is a general one. I wonder if it has been apparent in the many experiments carried out that there is a wall effect in the flow of wax suspensions or gels.

There are certainly indications of the effect in some of the graphs and from the variation of yield stress with roughness of the tubes. In the fundamental studies that Professor Sellers rightly feels are necessary, I think it would be valuable to study this effect. It can be done by varying the diameter of the flow tube and measuring viscosity. If there is a wall effect the viscosity will decrease as the diameter of the tube decreases. In concentric cylinder viscometers there may be a similar result. I think the results of such tests could be treated to give some information about the size of wax aggregates.

Professor E. S. Sellers: On the final point—wall effect and things like that. We are well aware of this, but do not know just what is happening in practice. We have made some experiments with different sizes of various tubes, just extruding the oil under various conditions through pipe. Let me confess that we have got virtually nowhere with them. In concentric cylinder viscometers, also, we are well aware that if the clearance between the cylinders is enough, then we may quite well have a situation where part of the oil is flowing, and part is gelled. But there again this matter has not been pursued. The work which is referred to here was done at the Admiralty Oil Laboratory, and the experimental conditions were very carefully selected so that the mathematical model which was put up, based on the rate theory of Eyring and others about the rate of breakdown and the simultaneous rate of build-up of wax crystals, could be investigated. What we put in here is a rather simplified version of that work. You are absolutely right that in the simplification, the p_e, which refers to elastic properties, is actually missed from this. It is not missed from the complete description which will be published in the *Journal of the Physical Society*.

On the question as to whether we get right down ultimately to a viscous state which is independent of the shear stress applied to the oil, that is a deduction from the manipulation of the data. Let me say again that in all these cases where one is trying to put up some rheological interpretation, first of all one has to put up a mathematical model, and the terms one uses are not always directly related in a one-to-one relationship with physical things with which we are acquainted. It is very difficult, for instance, to think of fuel oil having elastic properties. But certain behaviour of the fuel oil in the experimental rig at the Admiralty Oil Laboratory had to have this elastic term inserted in order to explain the experimental results. I know I have not answered the questions explicitly, but once again I must ask you to wait until all the work is published in its entirety. Meanwhile, all one can say, in terms of the model postulated, is that the results appear to justify the treatment which has been given here.

Dr C. M. Cawley: There are two things that I must do before we close the meeting. In the first place, I am sure you would wish me to express our warmest thanks to Professor Sellers and his colleagues, and the whole Panel who have carried out this work, for the preparation and presentation of the papers which provide a valuable record and have given us the excellent meeting to-day. I know that they have put a tremendous effort into the task.

I know you would wish me to thank them on your behalf and that you would wish to show your appreciation in the usual way. (Applause.)

There is one other matter. We have spoken about the quality of the work, and its value to the Admiralty, and we have spoken also during the day about the contributions made by the industry, and by a great many organizations and individuals, but I know that before the meeting closes Captain Stewart would like to express the Admiralty's great appreciation of the work which has been done and is still going on.

Captain W. R. Stewart: I should like to take this opportunity, more or less on behalf of the Admiralty, of saying what this work has meant to us over the last ten years. As was said earlier, it was, I think, more than ten years ago that we set in hand an investigation to find means to ensure that the fuel for the Navy, either aboard ship or ashore, should be pumpable by practical means (that is important) in any conditions which we had to meet. And of course, the object was to find a compromise between the fuel, as determined by specification, and the conditions of pumping and use, which depended on the design of the ship, and so on. And obviously, to be able to decide on such a compromise, one needs to know a great deal about the fuel, and about the conditions, and that really, as I see it, is what the work discussed to-day has been aiming at as far as the Admiralty is concerned.

The results of this work we have had very ably described to us to-day.

Panel F of AFLAC, who have arranged the carrying out of the work, have pursued the matter in a way which seems to us to be worthy of very high praise, and as you have already said, Mr Chairman, and is widely known, the work was a co-operative effort on the part of the oil industry and universities, and other Government agencies, and I would like to emphasize the Admiralty's great appreciation of the help that we have received from all these good people in what, in the initial stages, anyway, seemed a very difficult problem. I think that as a result of this Panel's work we know now very much more. I hesitate to say that from the Admiralty's point of view we know enough, because that would be bound to be disproved at the next AFLAC meeting. But I think that we do know now where a reasonable compromise should lie. Some things have changed, as has been clear in the discussion to-day. The quality of the oil we are getting has changed, and we are getting better oil. Matters now seem to us to be under control, and we feel that we have a reserve of knowledge against any difficulties which might arise in the future. For all this, we are most grateful.

CONTRIBUTED DISCUSSION

R. Tourret (Esso Research Ltd.): The symposium has provided an admirable outlet for the large amount of research work that has been carried out by AFLAC Panel F, much of it on site under adverse weather conditions. The results are very interesting, particularly in the sense of showing what factors affect the " structure " and of showing that methods such as pour point and yield point do not give data which are immediately relevant to this problem.

Some points occur to me as follows. The structure formed has been shown to be extremely sensitive (for instance, see comment by Ackroyd, Hosking, and Lowe) and relatively small changes in temperature produce marked changes in " structure." At the same time, the shifting of oil in bulk storage, once " structure " has formed, can be very difficult. Does this provide a clue as to how a depot may most conveniently shift bulk oil in such a condition? Normally a stress is applied by pumping—or attempting to pump. Would it be preferable to have a coil of piping inside the tank and pump hot—or cold—fluid round the coil so that the FFO may be heated—or cooled—to break up the structure locally to a sufficient extent to permit subsequent pumping? By this is not intended heated storage, but merely means to disturb the temperature enough to break the sensitive " structure " when, and only when, pumping is required. In any case, what is the procedure recommended for depot staff to deal with a tank full of FFO which is proving difficult to pump?

Wyllie and Jones describe the laboratory pumping rig very thoroughly, but I think it should be placed on record that the initial design requirements did not include item (*b*), pumping rates. This was added later after the major design features had been finalized. The internal storage tank was thus severely limited in size, and it is interesting to learn that it has been possible to operate the rig under pumping conditions for long enough to achieve steady flow, especially in view of how long it took before steady conditions were achieved in the field. If 400 gallons is taken as the usable capacity of the internal tank and 8 gallons/min a typical flow rate (see Tables III, IV, and V), then allowing for a gradual build-up to speed, the total pumping time must have been about one hour. That this period has been sufficient to allow steady flow conditions to become established is an important design parameter for any future rigs of this type.

In these laboratory tests experiments were carried out with oils said to be " gelled." These, in fact, were oils which had been cooled for periods up to a maximum of only one month. It has been shown (Ackroyd, Hosking, and Lowe) that an oil can still be forming gel for periods up to two years, at least in bulk storage. It has also been shown (Fig 1 of Wyllie and Taylor) that quite a high proportion of the time spent by an oil in bulk storage is at low temperature. The difference in time is therefore quite striking, especially in view of the comment on oil No. 22 that its " structure " did not quickly reform and the comment on oil No. 43 that its " structure " did not reform after ten days in Arctic waters. What evidence is there that a " structure " did in fact form in the laboratory rig after cooling for such a short period? Is it possible to say how much " structure " was present? Since it is evident that a good deal more " structure " might form after prolonged storage, would the results obtained on pumping rates be optimistic as regards pumping oils from tanks after long-term storage?

Wyllie and Jones appear to be a little critical of their pumping team, who abandoned the oil as " unpumpable " in Run 54 after 145 minutes had produced only 10 gallons. Earlier, they remark that ship's staff would not take too kindly to no measurable flow after 30 minutes or at the most one hour. It seems that their pumping team are to be commended for devotion to duty, well in excess of that expected of ship's staff!

Ackroyd, Hosking, and Lowe have shown that two oils steadily formed gel during two years surface storage. It is perhaps significant that of the oils referred to by Davenport and Russell (Table II), the two which had been stored in the depot longest (B and F) had a thick crust of gel. With oil F, which had been stored longest, the crust could support a brick. Older oils, which, however, had not been stored in the depot so long, had not developed these crusts. This suggests that the length of undisturbed storage is an important factor regarding gel formation. Further, if oils were not disturbed, gels might steadily build up over a considerable period, at least up to the five years which oil F had been stored for. What data have Ackroyd, Hosking, and Lowe that the two oils referred to in Fig 7 were " fully-aged " after only two years? Is there any limit to the amount of " structure " that can form? If the steady build-up of a gel over the years is a general feature of FFO's, perhaps the recommendation to Admiralty depot staff should be to turn over every tank once a year, even if only by pumping the oil from one tank to another. This might sufficiently disturb the oil to prevent the steady build-up of gel, especially since Davenport and Russell report that as far as could be seen any breakdown of viscosity (*i.e.* " structure ") occurred in the first few hundred feet of line, and since passing an oil through a pump will tend to break the " structure " down.

When considering the flow of water in pipes, it is customary to allow different flow factors for different kinds of pipes due to the different internal finishes. It might be expected that with oil pumping experiments, as described by Davenport and Russell, the importance of a surface finish would be greater, since the viscosity is greater. Is it possible to consider this factor?

Davenport and Russell report that large quantities of

air entered the line, far more than could be accounted for by release from the oil itself. It proved difficult enough to seal the laboratory pumping rig, although the pipework was comparatively small in length and bore, the pipes were comparatively high quality hot-finished steel pipe, and the whole system was new. It is questionable whether or not it would ever be possible to seal a depot system. Presumably the answer would be to make the test measurements on the pressure side, rather than on the suction side, despite the consequent difficulty in arranging a test circuit? Leaks, apart from valves, would then at least be visible.

The obstruction to flow that can be caused by air pockets in suction pipelines is commented on in the conclusions, and it is clear that at least one design rule for small pipe systems (as on turbines and internal-combustion engines, for instance) is valid for these large pipe systems—*i.e.* the amount of suction pipeline should be kept to the absolute minimum. Ideally, the pump should be in the oil in the tank, so that there is no suction line at all! Since "structure" is broken down appreciably by a pump, there would be a double advantage in such a siting!

Wyllie and Taylor refer to a viscosity calculator supplied to customers by a fuel supplier and say that it does not make any allowance for the development of "structure." This is hardly surprising, since the Admiralty is probably the only customer that leaves FFO in storage long enough for "structure" to develop! A special calculator would be required for Admiralty use incorporating time as a factor, perhaps by multiplying the viscosity by, say, 160 per cent for each year of undisturbed storage (see Fig 7 of Ackroyd, Hosking, and Lowe).

Wyllie and Taylor are to be commended, along with one or two other authors, in that they have bravely attempted to draw conclusions. It would have been more informative if all authors had done so. However, while their first conclusion—that a survey of temperature of the oil in the tank should be the first step in an examination for probable pumpability—may be technically correct, one wonders in fact in these days of missiles and atomic bombs if the depot staff will have time for such exercises if the oil is needed in an emergency. And surely the sole purpose of storing it is that it is in fact readily available in an emergency?

The whole collection of papers presented at this symposium forms an admirable collection of a lot of careful research work. However, there is danger of not seeing the wood for the trees. The *raison d'être* of AFLAC is to advise the Admiralty on fuel and lubricant matters. What advice can be given to the Admiralty on the points on which it is presumably interested:

(*a*) How can the Admiralty avoid purchasing oil which will gel, or prevent gel formation in oils it has purchased?

(*b*) If the oil gels, how can it be rapidly and surely pumped?

H. I. Fuller and K. A. Lammiman (Esso Research Ltd): The considerable amount of work done by the Panel to ensure the pumpability of Admiralty fuel oils has contributed much to the understanding of fuel oil handling. The Panel's investigations involved the study of several aspects of this subject—specifications, supply, storage, transfer, and use. Despite certain differences, we believe that the methods of sampling, examination, and testing developed by the Panel could be applied with advantage to commercial grades and conditions.

Generally speaking, Admiralty fuel oils are relatively light when compared with industrial grades. Equally, Admiralty storage conditions differ markedly from commercial practice. However, a particular aspect of the Panel's work, transfer in pipelines, is common to both Admiralty and commercial practice. The good agreement between the calculated and observed pipeline viscosities should do much to support the use of Poiseuille's equation when dealing with oils of comparatively high viscosity, at least under steady-state conditions. Nevertheless, the Panel will agree that a lot is not understood about the flow behaviour of oils in the pipe, such as, for instance, the nature of the flow pattern and the effect of air in the pipe. Indeed, in this connexion, observations during the full-scale trials would suggest that the effective capacity of many industrial pipelines could well be increased by the strategic siting of air vents.

As a further practical point, because much higher pressures can be achieved on the pressure side of the transfer pump, it may be deduced from the work reported that a gelled line may in some instances be cleared by "back pumping" with a comparatively small quantity of ungelled oil. Similarly, where the oil in both line and tank is very viscous there is a good chance that the increased shearing stress at the tank exit, after the line has first been cleared by back pumping, will enable the tank to be cleared too, the shearing of the oil as it leaves the tank ensuring that oil of pumpable viscosity enters the pipeline.

The Panel has quite rightly emphasized the importance of sampling techniques where oils with structure are concerned. This is a point that industry could well bear in mind, but probably of much greater importance where considerations of structure are involved are the structural changes which clearly take place in an oil between blending and transfer to the storage tank. Very little is known about changes which occur in this interval, and much needs to be done to determine the physico-chemical nature of residual fuel oils. A chemical approach to the problems of structural changes in fuel oil would be very interesting, as it could well lead to an understanding of such phenomena as inoculation and perhaps to the deliberate production of low-pour oils.

The predictive method evolved by the Panel (*i.e.* Method XV, which consists of a heat-treatment procedure followed by measurements of viscosity) relates to the particular grade of fuel oil used by the Navy. Little is known of its applicability to commercial grades. However, for many years the industry has placed what is now known to be undue reliance on pour point as a criterion of pumpability of residual fuel oils, and it may be that the present symposium will provide the impetus for a closer look at the position. In any event, the work of the Panel will clearly stand as a sound basis for extensive work by the industry for a long time to come.

R. J. Russell and T. C. Davenport: Mr Tourret points out that Ackroyd, Hosking, and Lowe have shown that relatively small changes of temperature produce marked changes in structure and suggests that use could be made of this effect to disturb the oil's structure in a tank to achieve good pumpability. Although this has not been tried on the large scale, we feel that in practice a suction heater should be all that is required to ensure pumpability with this type of fuel oil.

Mr Tourret asks what evidence there is that the structure developed in the Arctic rig is similar to that produced after long-term unheated surface storage. The Arctic rig was designed to simulate the conditions which may occur on board ship where an oil loaded from surface or underground storage might cool relatively slowly over

a period of time of the order of one month. Thus the structure developed might not be that of long-term storage. The rig results, however, probably also apply to the start-up of gelled surface pipelines where the oil is never left undisturbed for more than two months.

The suggestion is made by Mr Tourret that many of the oils tested on the large scale were not in their worst pumpability condition, since they had only been stored undisturbed for one or two years. Although this may be true in one or two cases, it is not confirmed by the work of Ackroyd, Hosking, and Lowe. This work, which has now been continued for four years, has shown that the aging of the oils was virtually completed in two years, since there was no increase in viscosity during the third and fourth year.

Friction factor curves (*e.g.* Moody, L. F., *Trans. Amer. Soc. mech. Engrs*, 1944, **66**, 671–84) show that surface finish is not of importance in laminar flow. In our large-scale work, which was always in the laminar flow region, this has been confirmed. However, laboratory work has shown that the yield value in capillary U-tubes is markedly affected by the wall material. There has been insufficient work to show whether this is equally true on the large scale.

It is not thought that there were any significant leaks of air into the line during the trials. Several backing-up tests were carried out on a completely closed line when all the valves were shut. In all these runs, after the initial backing-up flow, the flow rate dropped to zero, showing that any leaks were far too small to account for the air which accumulated during the course of a run.

D. Wyllie: Mr Tourret has raised a few interesting points regarding the behaviour of furnace fuel oil in storage. In these papers we have used the term "structure" to describe the condition of these fuels when they acquire markedly non-Newtonian characteristics. We do not regard oils as being "gelled" until they reach the semi-solid condition easily recognizable by the layman as such. In bulk storage tanks the rate of heat loss once gelation of the outer layer commences is so slow that the bulk oil cools only very slowly. In the laboratory pumping rig the dimensions of the cold room tank are very much less, and it was possible to cool both pipeline and cold room tank much quicker and reach the gelled state in under a month. The evidence for the existence of "structure" in the oils in this rig is the "gelled" appearance of the oil, its behaviour on start-up in the pipe, and its viscosity breakdown curves in the viscometers.

The work described covers the thought and action of the Panel over ten years. As knowledge grew there was inevitably a change in outlook. The laboratory pumping rig was, as Mr Tourret says, originally envisaged when the most important factor was thought to be yield value, but most of the instrumentation and the increase in size of the cold room tank was selected to permit pipe viscosity measurements. Run 54 was conducted while the time factor in the yielding of a pipeline was not so well appreciated as it is now. In some other runs pumping was continued for several hours.

With regard to the examination of oil in a depot to ascertain its pumpability, we do not anticipate that fuel will become unpumpable at short notice, and advance warning that any oil is developing undesirable features is given by storehousemen in routine inspections of stocks. We therefore expect to have an opportunity to examine any such oil in good time and know the best method of dealing with it. The commercial viscosity calculator we referred to was used solely as a reference line to show how far stocks deviate from the ideal.

It is anticipated that the new Method XV pumpability test, which was described in the paper by Ackroyd, Hosking, and Lowe, will largely eliminate oils having undesirable pumping characteristics. As a further safeguard, heating facilities and other modifications are being installed to aid the handling of the less pumpable fuels.

E. W. Billington (Admiralty Oil Laboratory): If the assertion of Mr Davenport concerning the yield value, namely, that "once the oil has yielded and flow has commenced there is no measurable yield stress" is valid, then the question arises of why the system continues to exhibit a time-dependent resistance to flow with continuous shearing.

In reply to Mr Hutton, the assumption that the time-dependent yield value $p_y(t)$ is zero after an infinite time of shearing is justified only if the absolute rate of generation of structure with time of storage is never much smaller than the absolute rate of breakdown under an applied stress; this condition is satisfied for the oils examined, the rate of generation of structure being about a hundred times smaller than the rate of breakdown.

The equation $p(t) = p_s(t) + p_\epsilon(t)$ has been applied to measurements at (1) constant rate of shear and (2) at constant applied stress. For measurements at constant rate of shear the elastic stress component p_ϵ is set equal to zero; for measurements at constant applied stress (to be published in *Proc. Phys. Soc.*) the equation

$$\eta_t = \frac{p - p_\epsilon(t)}{\dot{S}t}$$

is used to calculate a viscosity which is then correlated with the measurements at constant rate of shear.

The compounding together of the "yield value–time-of-shearing" curves, for the different values of the rate of shear, to an accuracy of ± 7 per cent over a range of yield values from 2 dynes cm^{-2} to 1320 dynes cm^{-2} for a time of shearing extending from zero to one hour, is taken as evidence that slip at the wall of the viscometer cylinders had not occurred in these experiments.

IP STANDARDS

A Correction

THE correct designation of the method for Rust Preventing Characteristics of Steam Turbine Oil which appears in the 19th edition of "IP Standards for Petroleum and Its Products" is IP 135/60. The terms in which the results are reported have been amended considerably from the previous versions.

OBITUARY

STANLEY FRANCIS BIRCH

1899–1960

In the untimely death of Dr S. F. Birch on 25 March at the relatively early age of 60, the British petroleum industry has lost one of its most outstanding chemists, indeed, one of international fame in the fields of hydrocarbon chemistry and sulphur compounds. Apart from these activities, his name will always be linked with the original conception of the alkylation process, in the development of which he took the leading part.

It was at St Paul's School, Hammersmith, where his abiding interest in organic chemistry was born, and after graduating with research honours from Imperial College in 1923 Dr Birch joined the then "infant" BP research organization at Sunbury-on-Thames. He commenced his life's work with a thorough technical study of the hypochlorite process for the desulphurization and sweetening of light petroleum products. This work inevitably focused his attention on sulphur compounds, and it was not long before his publications on these subjects were receiving world-wide acknowledgment and appreciation.

During his many years at Sunbury, by his example and enthusiasm, he steadily gathered around him a staff of able and keen research chemists who helped to extend his original work and firmly established his Chemical Research Section as one of undoubted pre-eminence in the scientific world. His contributions to the scientific and technical press are too numerous to mention here, but they are all characterized by painstaking care, excellent presentation, and accuracy in the information provided.

His readiness to impart his knowledge to younger research workers could always be counted upon, and he was indefatigable in his efforts to correct erroneous trends and opinions. In 1957, in order to make full use of his knowledge and ability, he relinquished the direction of his famous research section and became one of Sunbury's research associates, thereby widening the service he was able to afford to other technical interests. More recently he extended his research association to the rapidly growing BP Petroleum Chemicals Department, where his great knowledge of organic chemistry and his far-sightedness proved to be of inestimable value.

Dr Birch was also an active member of the Institute's Hydrocarbon Research Group, being chairman of its Hydrocarbon Chemistry Panel from its inception in 1944 as the Hydrocarbon Synthesis Panel, with only a short break.

His loss to the BP Group will be keenly felt, particularly by those who had relied so much on his vast chemical knowledge and readily-given help in elucidating their problems. His many friends, in Britain and in the United States, will mourn his departure from among us.

W. H. T.

I have read with interest and appreciation the account of the career of S. F. Birch by his old companion W. H. Thomas.

Birch came to us at Sunbury very early in the history of that great research centre. He arrived in 1923 fresh from a good stable—that of the late Sir Jocelyn Thorpe at the Royal College of Science, where he had acquired much of the technique of his famous master. He was at once put on to study the thio-derivatives in Persian gasoline and succeeded in unravelling their complexity. Later he was concerned with the development of the hypochlorite process for their removal by simple oxidation and travelled widely in the U.S.A. under the ægis of our friend Dr B. T. Brooks—an American chemist of international reputation. There he met many scientific colleagues with whom he established lifelong friendships. On his return he embarked upon his famous researches on hydrocarbon chemistry, especially with reference to the reactivity of the tertiary carbon atom. This work culminated in the alkylation process so well known as the source of supremely high octane aviation spirit.

Birch was cut off at his prime. He would undoubtedly have done even greater things had he been spared. His intellect was of the highest order and matched only by a thoroughness of his mental discipline.

I lament in his passing the loss of one who was a pupil, a collaborator, a colleague, and a friend.

He will be mourned not only by his old colleagues at Sunbury but by all who came in contact with him. Of him can truly be said *integer vitae—scelerisque purus.*

A. E. D.